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This report describes the factors that determine the extent of sorption of organic compounds that are representative of coal conversion waste streams. The compounds, all radiolabeled, were acetophenone; 1-naphthol; pyrene; 7,12-dimethylbenz(*a*)anthracene; 3-methylcholanthrene; dibenz(*a*,*h*)anthracene; acridine; 2,2'-biquinoline; 13*H*-dibenzo(*a*,*i*)carbazole; dibenzothiophene; benzidine; 2-aminoanthracene; 6-aminochrysene; and anthracene-9-carboxylic acid. Batch equilibrium isotherms were determined for each compound on 14 sediments and soils that had been collected from the Missouri, Illinois, Mississippi, and Ohio rivers and their watersheds. Laboratory procedures for determining octanol-water partition coefficients and water solubilities were developed and then performed on the compounds.

The sorption constants were correlated with soil and sediment properties and with the water solubilities and octanol-water partition coefficients of the compounds. Regression equations were developed that allow prediction of a hydrophobic compound's linear partition coefficient from knowledge of the compound's octanol-water partition coefficient or its water solubility and the organic carbon content of the sediment or soil.

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SORPTION PROPERTIES OF SEDIMENTS AND ENERGY-RELATED POLLUTANTS

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FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Environmental Processes Branch studies the microbiological, chemical, and physico-chemical processes that control the transport, transformation, and impact of pollutants in soil and water.

Efforts to achieve our national goal of energy independence will require increasing use of our country's vast domestic coal reserves. The combustion of coal or its conversion to a gaseous or liquid fuel, however, can release numerous organic compounds that are potentially toxic, carcinogenic, or mutagenic. This report examines the sorption properties of several energy-related pollutants on sediments. Information on these properties is needed to predict the movement of the compounds in aquatic systems so that potential environmental problems can be anticipated.

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Director
Environmental Research Laboratory
Athens, Georgia

ABSTRACT

This report describes the factors that determine the extent of sorption of organic compounds that are representative of coal conversion waste streams. The compounds, all radiolabeled, were acetophenone, 1-naphthol, pyrene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholanthrene, dibenz[*a*,*h*]anthracene, acridine, 2,2'-biquinoline, 13*H*-dibenzo[*a*,*i*]carbazole, dibenzothiophene, benzidine, 2-aminoanthracene, 6-aminochrysene, and anthracene-9-carboxylic acid. Batch equilibrium isotherms were determined for each compound on fourteen sediments and soils that had been collected from the Missouri, Illinois, Mississippi and Ohio rivers and their watersheds. Laboratory procedures for determining octanol-water partition coefficients and water solubilities were developed and then performed on the compounds.

The sorption constants were correlated with soil and sediment properties and with the water solubilities and octanol-water partition coefficients of the compounds. Regression equations were developed that allow prediction of a hydrophobic compound's linear partition coefficient from knowledge of the compound's octanol-water partition coefficient or its water solubility and the organic carbon content of the sediment or soil. Regression equations were tested on independent data sets from the literature for the adsorption of parathion and a variety of halogenated hydrocarbons. Observed values for these compounds were in good agreement with values predicted by the regression equations.

This report was submitted in partial fulfillment of Contract No. 68-03-2555 by the Department of Agronomy and the Institute for Environmental Studies of the University of Illinois at Urbana-Champaign under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period from July 1, 1977 to December 31, 1979.

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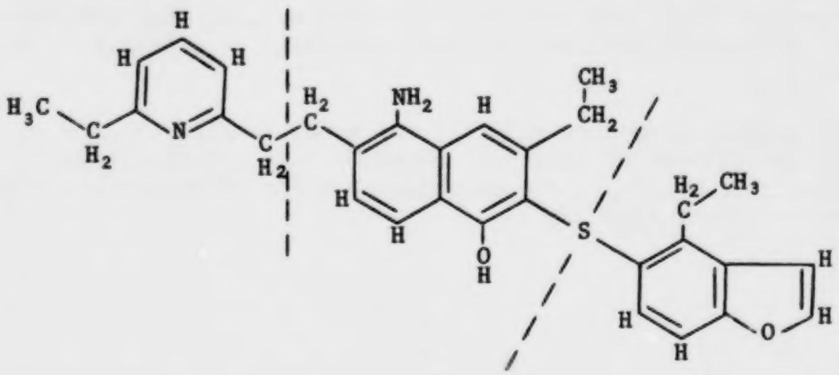
SECTION 1

INTRODUCTION

The contract contained two basic tasks. The first was to perform a literature review covering the theory of sorption and the sorption properties of energy-related compounds. This literature review, *Adsorption of Energy-Related Organic Pollutants* (EPA-600/3-79-086), has been published by the U.S. Environmental Protection Agency. The second task involved determination of sediment/soil and pollutant properties that control sorption of compounds typical of coal conversion effluent streams.

With the current proposed increase in the use of coal for energy production, there is concern for the environmental effects of pollutants that are produced at various stages of coal mining and processing. Coal is an extremely complex organic polymer interlaced with inorganic trace impurities. The following figure shows a typical chemical representation of the coal polymer (1).



It is apparent that the various fragments of the coal structure include a tremendous variety of polycyclic aromatic, heterocyclic aromatic, phenolic, amine, quinone, sulfur, nitrogen and other compounds. The characterization of some of the organic wastes from coal conversion has been reported for pilot plant studies. Forney *et al.* (2) identified some of the major organic constituents of tars produced by the Synthane coal gasification process. Schmidt *et al.* (3) has analyzed process water for major organic constituents.

Coal conversion processes result in extremely large gaseous and aqueous effluent streams (4). In addition to the wastes produced directly by the conversion process, unspecified large quantities of water are produced constituting the leachate from coal storage, solid wastes and particulates. When effluent streams this large are produced, significant quantities of constitutents can be placed into the environment.

Introduction of the effluent streams into the environment will result in exposure of the organic pollutants to sediments or soils and their subsequent sorption to the extent that it is chemically or physically dictated. Sorption results in lower aqueous concentrations of the pollutants. Hence, potential physiological activities (5) and release of mobilities within the environment as well as other effects may be decreased. The extent of sorption of organic materials by sediments and soils is dependent upon the nature of both the sorbent (soil or sediment) and the sorbate (pollutant).

In a number of studies of organic pesticide sorption by soils, sorption has been correlated with humus content, clay mineral type and content, texture, pH and hydrous oxide content. The nature of the organic molecule, whether it is a cation, anion or neutral molecule, its water solubility or octanol-water partition coefficient, and its polarizability are a few of the properties of the sorbate that interact with the solid phase to determine the amount of sorption.

The sediments and soils used in this research were collected from the Missouri, Mississippi, Illinois and Ohio rivers and their watersheds. These samples provided a wide range in properties such as organic matter content, clay content and type, and hydrogen ion activity (pH) that are known to affect sorption. Sampling sites were in close proximity to potential coal gasification areas (6).

The organic compounds selected for study (Table 1.1) are representative of many of the classes of compounds found in coal conversion waste streams. In addition, they encompass a wide range of compound properties that have been shown to affect sorption.

TABLE 1.1. COMPOUNDS SELECTED FOR STUDY

Polynuclear Aromatic Hydrocarbons
Pyrene
7,12-Dimethylbenz[*a*]anthracene
Dibenz[*a,h*]anthracene
3-Methylcholanthrene

Aromatic Amines
Benzidine
2-Aminoanthracene
6-Aminochrysene

Aromatic Alcohols
1-Naphthol

Nitrogen and Sulfur Heterocyclics
Dibenzothiophene
Acridine
2,2'-Biquinoline
13*H*-Dibenzo[*a,i*]carbazole

Aromatic Ketones
Acetophenone

Organic Acids
Anthracene-9-carboxylic Acid

SECTION 2

CONCLUSIONS

Sorption results when a solution component is concentrated at an interface (7). For sediment-water or soil-water systems the interface of interest has primarily been the solid-liquid interface. Sorption occurs when the forces of attraction between the sorbing species and the solid surface overcome both the forces of attraction between the sorbing species and the solvent (8) and any repulsive forces between the sorbate and sorbent (9,10). The sorbing species is called the solute when it is in solution and the sorbate when it is sorbed to the sorbing surface (sorbent).

For organic compounds there are two general cases where the affinity of the sorbate for the sorbent is greater than the affinity of the solute for the solvent and significant sorption results. In the first case, there is a strong specific interaction (coulombic attraction, ligand exchange or hydrogen bonding (11)) between the sorbate and the sorbent, and these forces of attraction overcome even a fairly strong attraction of the solute to the solvent. The sorption of organic cations or polar organic molecules by swelling clay minerals (12) is an example of this type of sorption. The sorption of benzidine (Section 4.3) from acid solutions is an example from this research (13).

Sorption that is characteristic of the second case results not because of a large specific sorbate-sorbent interaction but rather because of a weak solute-solvent interaction. In this case, even a weak positive sorbate-sorbent interaction can overcome an extremely weak solute-solvent interaction and result in the compound being removed from solution.

The weak solute-solvent interaction, that is, the low water solubility or hydrophobic nature of many organic molecules, is the result of a large decrease in entropy of the system upon solvation (14), coupled with an absence of hydrophilic functional groups or at least a dominance of the hydrophobic portion of the molecule. The attraction between a hydrophobic organic molecule and the sorbent is not the result of specific interactions as in the first case, but rather of general interactions between the sorbate and sorbent such as van der Waals forces (14). The sorption of aromatic hydrocarbons by soil or sediment humic materials is an example of this type of sorption (15,16,17,18). This second case of sorption has been referred to as hydrophobic sorption because of the emphasis on the role of the weak solute-solvent (water) interaction (14,16).

Hydrophobic sorption increases as compounds become less and less polar, that is, as molecular weights, molecular volumes or carbon numbers increase or as water solubilities decrease (15,18). Hydrophobic sorption has been shown to be highly correlated with the organic carbon content of the soils or sediments while at the same time relatively independent of other sorbent properties (15,16,17,18). When sorption of hydrophobic compounds is expressed as a function of the organic carbon content of the soil or sediment, a constant, Koc, is generated which is a unique property of the compound being sorbed (11,15,16,17,18):

$$\text{Koc} = \frac{\text{Kd}}{\%\text{OC(decimal equivalent)}} \qquad (2\text{-}1)$$

where Koc is equal to the Freundlich constant (Kd) divided by percent organic carbon (decimal equivalent) in the respective soil or sediment. Thus, for these compounds, Kd values may vary dramatically from soil to soil or sediment to sediment, but the Koc values converge toward a value that is constant across all soils and sediments. For linear isotherms ($1/n = 1$) Kd may be expressed on a mass basis or a molar basis; for nonlinear isotherms ($1/n \neq 1$) Kd must be expressed on a molar basis (19). For linear isotherms the best fit is often achieved by forcing 1/n to be equal to one. This has the effect of expressing all the variation between isotherms in one constant (Kd). Small changes in 1/n can result in large differences in Kd, masking any potential correlation of Kd with sorbate or sorbent properties.

The partitioning of organic compounds between water and an organic solvent, usually octanol, has been correlated with the extent of hydrophobic sorption. Increasing octanol-water partition coefficients (Kow values) for a series of compounds have been related to increased sorption when sorption is expressed in terms of Koc values (15,18):

$$\text{Kow} = \text{conc. cpd in octanol/conc. cpd in water} \qquad (2\text{-}2)$$

where the octanol and water phases have been equilibrated to allow partitioning of the compounds between the two phases.

A summary of the results of the sorption experiments is given in Table 2.1. The Koc values were calculated from a regression (20) of the compounds' linear or molar partition coefficients against the respective organic carbon contents (decimal equivalents) of the 14 sediment and soil samples used in the sorption experiments. The Koc values ranged from a low of 35 for acetophenone to a high of 1,668,800 for dibenz[*a,h*]anthracene. The water solubilities varied from 5,440 μg/ml for acetophenone to 0.00249 μg/ml for dibenz[*a,h*]anthracene. The octanol-water partition coefficients went from a low of 38.6 for acetophenone to a high of 3,170,000 for dibenz[*a,h*]anthracene. Individual Kp values and a more detailed discussion of the factors affecting the sorption of the respective compounds are given in the following sections.

Figure 2.1 presents the relationship of Koc and Kow for the compounds studied as part of this contract with the exception of benzidine which is protonated at low pH and then behaves as an organic cation (see Section 4.3). The sorption data for the compounds studied by Karickhoff *et al.* (15) are also included in order to expand this relationship to a greater number and

TABLE 2.1. Koc VALUES AND THEIR CORRELATION COEFFICIENTS FOR THE SORPTION OF ENERGY-RELATED ORGANIC POLLUTANTS BY SOILS AND SEDIMENTS; OCTANOL-WATER PARTITION COEFFICIENTS AND WATER SOLUBILITIES OF THE SAME COMPOUNDS

Compound	Measured Koc values from isotherms[a] Koc	r^2	Octanol-water partition coefficient[b] Kow ± S.D.	Water Solubility[c] S ± S.D. (μg/ml)
Pyrene	63,400	0.965	124,000 ± 11,000	0.135 ± 0.013
7,12-Dimethylbenz[*a*]anthracene	225,308	0.908	953,000 ± 59,000	0.0244 ± 0.0042
Dibenz[*a,h*]anthracene	1,668,800	0.783	3,170,000 ± 883,000	0.00249 ± 0.00081
3-Methylcholanthrene	1,244,046	0.705	2,632,000 ± 701,000	0.00323 ± 0.00017
Dibenzothiophene	11,230	0.904	24,000 ± 2,200	1.47 ± 0.14
Acridine	12,910	0.934	4,200 ± 940	38.4 ± 4.5
2,2'-Biquinoline	10,404	0.922	20,200 ± 2,200	1.02 ± 0.12
13*H*-Dibenzo[*a,i*]carbazole	1,055,926	0.830	2,514,000 ± 761,000	0.0104 ± 0.0041
Acetophenone	35	0.898	38.6 ± 1.2	5,440 ± 71
1-Naphthol	522	0.876	700 ± 62	866 ± 31
Benzidine	NA[d]		46.0 ± 2.2	360 ± 8.0
2-Aminoanthracene	28,129	0.871	13,400 ± 930	1.30 ± 0.159
6-Aminochrysene	143,355	0.949	96,600 ± 4,200	0.155 ± 0.018
Anthracene-9-carboxylic acid	422	0.751	1,300 ± 180	85.0 ± 1.9

[a] Koc values and correlation coefficients (r^2) calculated from a regression of Kp against %OC (decimal equivalent).

[b] Determined by the procedure given in Section 5.2.

[c] Determined by the procedure given in Section 5.3.

[d] NA = not applicable: non-hydrophobically sorbed compound; Koc values did not converge.

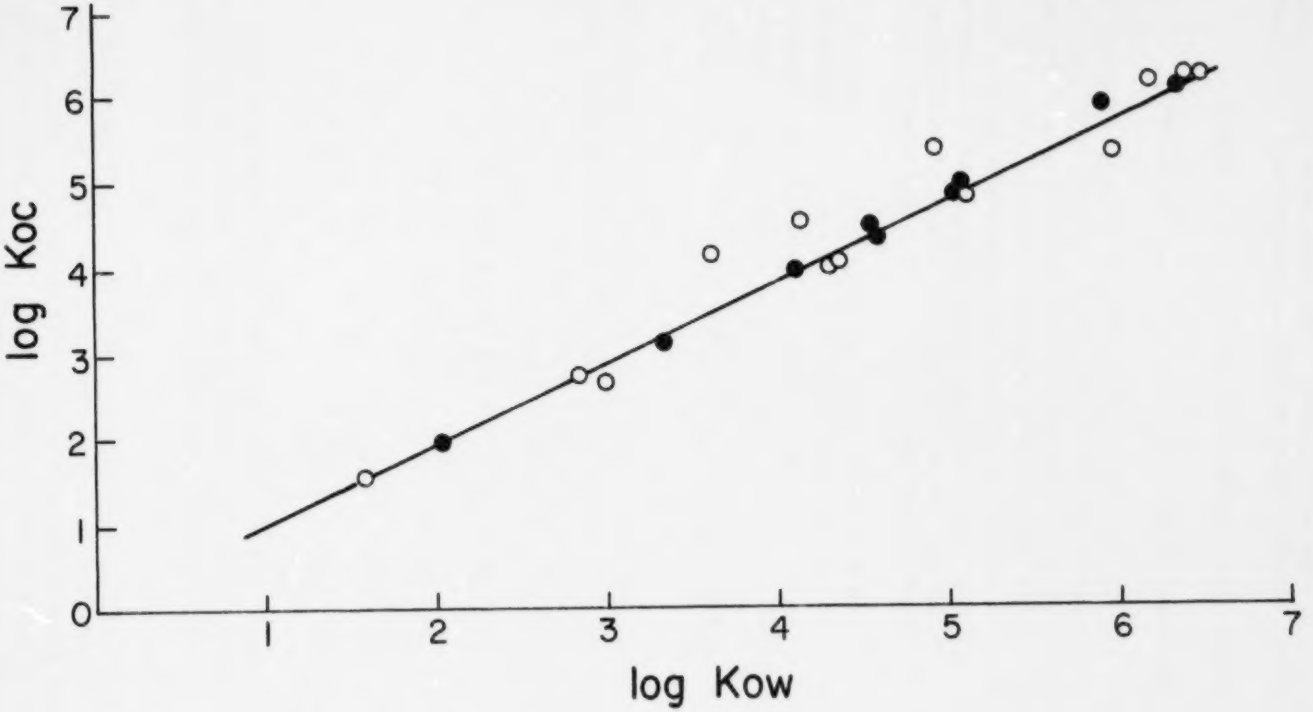


FIGURE 2.1. RELATIONSHIP BETWEEN Koc AND OCTANOL-WATER PARTITION COEFFICIENT (Kow) OF ENERGY-RELATED ORGANIC POLLUTANTS

● Data from Karickhoff *et al.* (15); ○ Data from this investigation.

variety of compounds. A similar but inverse relationship between Koc and water solubilities (S) was found for both sets, as illustrated in Figure 2.2.

The Koc values of the hydrophobic compounds were highly correlated with their respective water solubilities or octanol-water partition coefficients.

$$\log Koc = -0.686 \log S(\mu g/ml) + 4.273 \qquad r^2 = 0.933 \qquad (2\text{-}3)$$

$$\log Koc = \log Kow - 0.317 \qquad r^2 = 0.980 \qquad (2\text{-}4)$$

The behavior of the aromatic hydrocarbons in both this and the Karickhoff *et al.* (15) study is not unexpected. These compounds are highly hydrophobic, lacking ring constituents or functional groups that could significantly modify their hydrophobic nature. However, the fact that the heterocyclic compounds studied as well as the compounds with reactive functional groups, with the exception of benzidine, were also hydrophobically sorbed strengthens the concept that the solute-solvent interaction is the dominant interaction controlling the sorption of these compounds.

Equations 2-3 or 2-4 coupled with equation 2-1 represent a powerful tool that can be used to predict the sorptive behavior of hydrophobic compounds. Equation 2-3 or 2-4 can be used to predict the compound's Koc value based on the water solubility or octanol-water partition coefficient. The Koc value and the organic carbon content of the sorbent (soil or sediment) can then be used with equation 2-1 to predict the linear partition coefficient or molar Freundlich Kd value.

The use of equations 2-1, 2-3, and 2-4 can be illustrated by calculating the Koc value of parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate). Parathion ($C_{10}H_{14}NO_5PS$) has a molecular weight of 291 and a reported water solubility of 12.9 µg/ml (21).

$$\log Koc = -0.686 \log S + 4.273$$

$$\log Koc = -0.686 \log(12.9) + 4.273$$

$$\log Koc = 3.511$$

$$Koc = 3244$$

In order to check the validity of the calculated Koc value, individual Kd values were calculated for the samples used by Wahid and Sethunathan (21) and predicted Kd values compared with their measured mass Kd values (Table 2.2).

Measured and predicted sorption constants were in good agreement and a regression of the predicted Kd values for the sorption of parathion against the measured values gave a correlation coefficient of 0.984. Regression of the measured Mass Kd values against %OC (Table 2.2) gave a Koc value of 3329 which is in excellent agreement with the predicted Kd value of 3244.

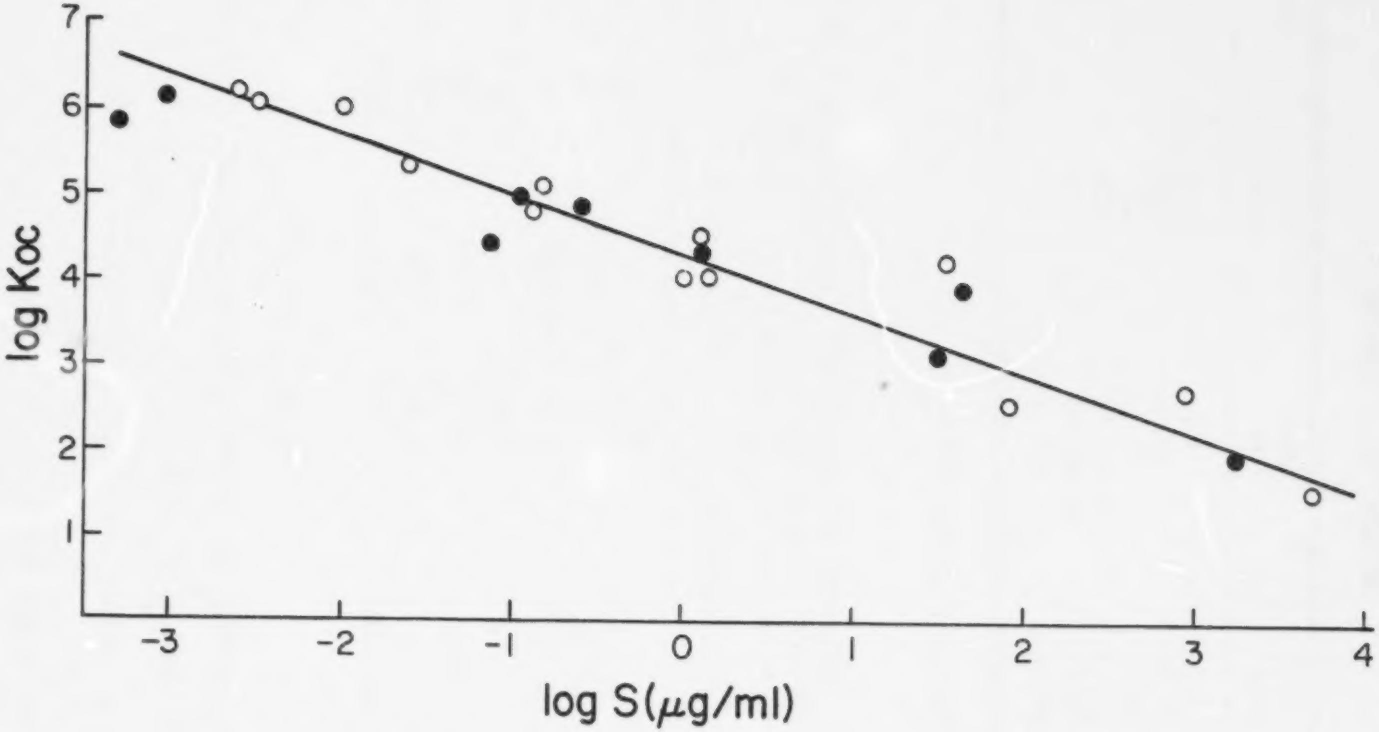


FIGURE 2.2. RELATIONSHIP BETWEEN Koc AND WATER SOLUBILITY (S) OF ENERGY-RELATED ORGANIC POLLUTANTS

● Data from Karickhoff *et al.* (15); ○ Data from this investigation.

TABLE 2.2. PREDICTED AND MEASURED Kd VALUES FOR THE SORPTION OF PARATHION

Sample	%OC	Mass Kd	1/n	Predicted Kd[a]
10	0.44	7.67	1.04	14.27
8	0.94	12.30	1.05	30.49
11	1.67	38.02	1.11	54.17
13	3.21	125.90	1.05	104.13
15	4.77	213.80	1.03	154.70
14	14.31	457.10	1.02	464.21

[a] Kd = Koc x %OC (decimal equivalent).

TABLE 2.3. PREDICTED AND MEASURED Koc VALUES FOR THE SORPTION OF HALOGENATED HYDROCARBONS BY WILLAMETTE SILT LOAM (1.6% ORGANIC MATTER, 0.84% ORGANIC CARBON)

Compound	Measured Kd[a]	Measured Koc[b]	Solubility (μg/ml)	Predicted Koc[c]
1,2-Dichloroethane	0.30	36	8,450	38
1,2-Dichloropropane	0.43	51	3,570	68
1,2-Dibromoethane	0.58	69	3,520	69
1,1,2,2-Tetrachloroethane	0.74	88	3,230	73
1,1,1-Trichloreoethane	1.66	198	1,360	133
1,2-Bromo-3-chloropropane	1.20	143	1,230	142
1,2-Dichlorobenzene	2.88	343	148	608
Tetrachlorethane	3.36	400	200	495

[a] Kd = G x 0.016; Chiou *et al.* (22).

[b] Koc = Kd ÷ 0.0084

[c] log Koc = -0.686 log S + 4.273

A second example of the utility and versatility of these equations is given by comparing predicted Koc values with measured Koc values from a study by Chiou *et al.* (22) on the sorption of a series of halogenated hydrocarbons (Table 2.3).

Correlation of the predicted Koc values with the measured values obtained by Chiou *et al.* gave a correlation coefficient of 0.931. The study of Chiou *et al.* illustrated the relationship of sorption and water solubility for one soil. The present study illustrates that this relationship can be extended to other classes of compounds and to other soils and sediments.

Equations 2-1, 2-3 and/or 2-4 have tremendous potential value in calculating sorption constants for the great number of organic materials where sorption data do not exist. Where sorption constants exist for a given situation, these relationships allow extension to other soils and sediments. The predicted Koc and Kp values are good first-order approximations, but they should eventually be verified by actual sorption studies.

The limits of the validity of the Koc, water solubility, octanol-water partition coefficient and organic carbon relationships (hydrophobic sorption) are not fully known. It has been demonstrated (see Section 4.2) that the limits are a function of both sorbate and sorbent properties. The concept of hydrophobic sorption may not be valid for compounds that contain hydrophilic functional groups. The presence of such groups may simultaneously increase solubility and decrease sorption, thus maintaining the established Koc-water solubility relationship (e.g., 6-aminochrysene or 2-aminoanthracene), or they may increase solubility and dramatically increase sorption by forming a cation as was the case with benzidine. It also appears that the concept of hydrophobic sorption may not be valid for sediments and soils that have low organic carbon contents in combination with medium to high swelling clay contents, particularly for compounds with low Koc values (see Section 4.2).

SECTION 3

RECOMMENDATIONS

Additional research needs to be conducted to better define the adsorbate and adsorbent properties where hydrophobic adsorption is the dominant adsorption process. If the Koc-Kow relationship (equation 2-3) and/or the Koc-S relationship (equation 2-4) are to provide as much possible information about the multitude of existing or new organic compounds, the limits of validity of the two equations must be defined.

There appears to be no maximum Kow value nor minimum water solubility where the relationships are not valid other than the limits imposed by analytical sensitivity. In fact, for very insoluble organics where the limits of analytical detection are approached in sorption experiments and where impurities and degradation products present very difficult problems, the Koc-Kow and Koc-S relationships may provide more reliable numbers than the actual sorption experiments. The existing data suggest that there should exist a minimum Kow value or maximum solubility such that compounds with greater Kow values or lower water solubilities will be strictly hydrophobically sorbed. For compounds with lower Kow values or higher water solubilities the compounds may be strictly hydrophobically sorbed independent of soil properties other than organic carbon or the compounds may be hydrophobically sorbed only by selected soils and sediments.

The acetophenone and 1-naphthol data suggest that the ratio of organic carbon to montmorillonite clay content may provide a method of predicting when hydrophobic sorption will dictate the behavior of a compound. These compounds were strictly hydrophobically sorbed above an organic carbon to montmorillonite ratio (%OC ÷ % montmorillonite) of 0.10 regardless of the nature of the soil or sediment. The relationship between this ratio and hydrophobic sorption needs further study to better define the critical ratio, if one exists.

Much of the existing data in the published literature are in terms of mass Kd or Kp values. It is recommended before equations 2-3 and 2-4 are used that data be either in the form of linear Kp values or converted to molar Kd values by the relationship of Osgerby (19):

$$\text{Molar Kd} = \frac{\text{Mass Kd} \times \text{Mol. wt}^{1/n}}{\text{Mol. wt}} \qquad (3\text{-}1)$$

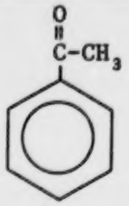
SECTION 4

LABORATORY INVESTIGATIONS

4.1. ACETOPHENONE

Acetophenone was chosen to represent one class of compounds, the aromatic ketones, which have been shown to be present in coal gasification wastes (2). The physical properties of acetophenone are given in Table 4.1.

TABLE 4.1. PHYSICAL PROPERTIES OF ACETOPHENONE

Structure	
Molecular weight[a]	120.15
Melting point (°C)[a]	19-20
Boiling point (°C)[a]	202
Density[a]	1.03
Flash point (°C)[a]	82
Heat of vaporization, ΔHv (cal/gmol)[b]	11,731.5

[a] Aldrich catalog, 1979-80

[b] CRC Handbook, 1975-76

Water solubility was determined to be 5,440 μg/ml by the procedure given in Section 5.3. The octanol-water partition coefficient of acetophenone was determined to be 38.6 by the procedure given in Section 5.2.

Batch equilibrium sorption isotherms were determined using ^{14}C-labeled acetophenone (>99 percent pure) obtained from ICN Pharmaceuticals, Inc., and unlabeled acetophenone (>99 percent pure) from Eastman Kodak Co. Purity was verified using thin-layer chromatography (see Section 5.1.2). A stock solution (4,154 μg/ml) was prepared in ultrapure distilled water. The sorption isotherms were determined in triplicate on a 2:5 sample to solution ratio (10 g soil/sediment sample and 25 ml acetophenone solution) with initial concentrations of 138, 277, 554, 831 and 1,108 μg/ml. Samples were equilibrated in stainless steel centrifuge tubes (aluminum foil-covered lids) in a temperature-controlled shaking water bath at 25°C for 24 hours. Initial and final concentrations of acetophenone in the solution phase were determined by liquid scintillation counting. The concentration of acetophenone in the soil or sediment samples (μg/g) was determined by difference. A ^{14}C mass balance was determined on selected samples to verify that there was no loss of compound from the system. Gas chromatography was used to determine if a significant quantity of the acetophenone had been degraded. Retention times for the parent compound and the compound present in the solutions equilibrated with soil or sediment samples were identical, and no unidentified peaks were observed. This was taken as evidence that no degradation of acetophenone had occurred.

Sorption of acetophenone on the sediment and soil samples followed a linear trend over the entire concentration range studied. Representative isotherms are shown in Figure 4.1. Average values of the sorption isotherm data for each soil and sediment are given in Table 4.2. The sorption isotherms were described by the following equation:

$$Cs = Kp \cdot Cw \qquad (4\text{-}1)$$

where Cs is the amount of compound sorbed by the soil or sediment in μg/g, Cw is the equilibrium solution concentration in μg/ml, and Kp is the linear partition coefficient.

The linear partition coefficients and Koc values for the sorption of acetophenone are given in Table 4.3. The Kp values varied from a low of 0.07 for sample 8 to a high of 0.89 for sample 4.

Simple correlations between Kp and selected soil properties were determined. These data indicated that the correlation between Kp and percentage organic matter was highly significant at the 1 percent level of probability. The other factors tested, i.e., pH, CEC, % clay and % montmorillonite, were nonsignificant. Regression of Kp against organic carbon content (decimal equivalent) produced the following equation:

$$Kp = 35.0(\%OC) \qquad r^2 = 0.898 \qquad (4\text{-}2)$$

where 35.0 is the Koc value for acetophenone.

The Koc values obtained for the individual soils and sediments were closely grouped around the regression value of 35.0 with the exception of samples 6 and 9; these two samples have the smallest percent organic carbon to percent montmorillonite ratios.

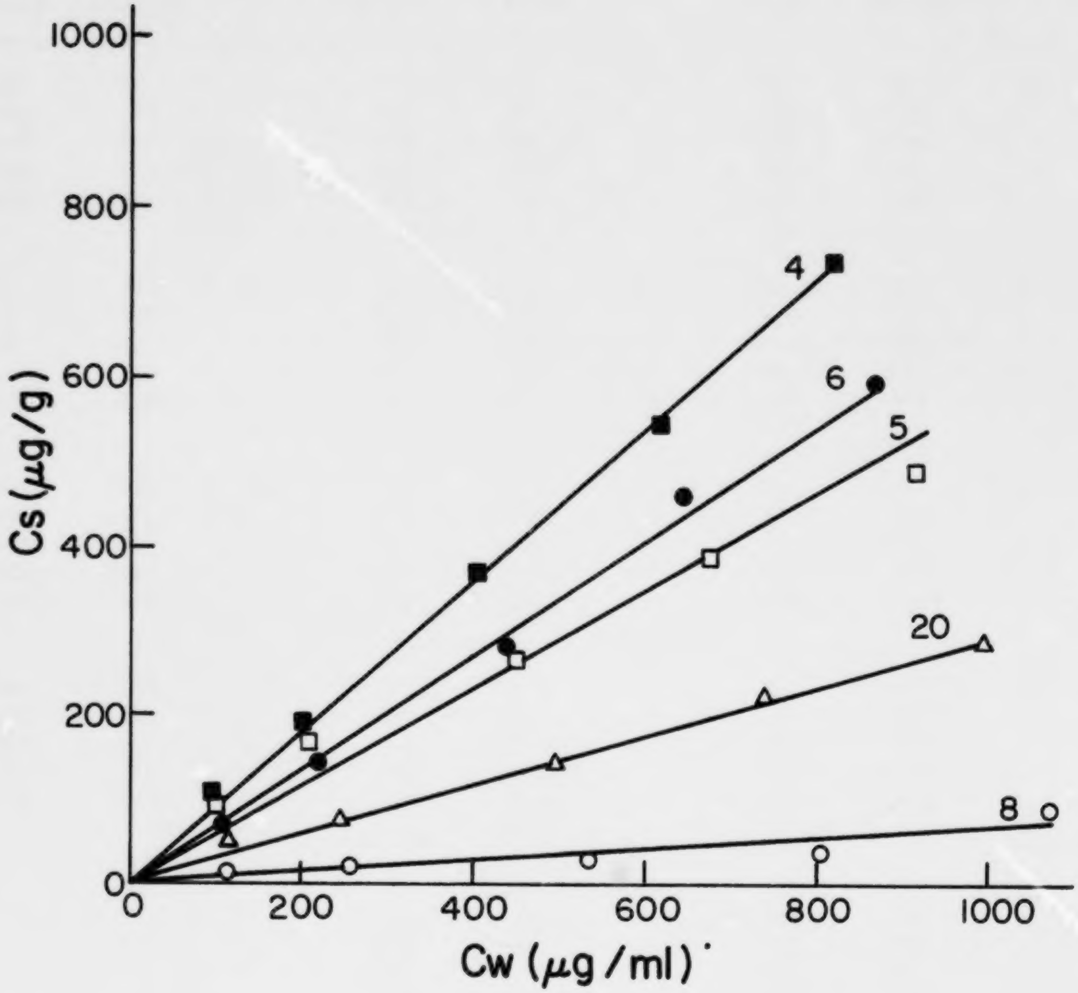


FIGURE 4.1. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF ACETOPHENONE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.2. ACETOPHENONE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (μg/ml)	Cs[c] (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)
B2	112	67	4	95	109	5	97	104
	233	110		198	199		211	164
	475	198		405	372		448	263
	704	319		615	538		676	387
	943	411		816	728		916	480
6	111	67	8	122	11	9	135	8
	219	144		267	25		265	30
	444	275		541	30		539	38
	645	465		814	40		811	50
	870	594		1070	94		1061	117
14	130	21	15	118	51	18	121	45
	260	44		243	86		251	64
	519	87		493	153		493	151
	792	98		756	187		747	209
	1062	115		1004	261		983	312
20	119	49	21	90	121	22	103	89
	247	73		196	203		220	143
	499	136		417	341		461	233
	742	223		629	504		681	374
	996	279		822	714		921	466
23	92	117	26	93	133			
	201	189		203	185			
	425	323		439	287			
	649	456		652	448			
	885	558		884	558			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

TABLE 4.3. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF ACETOPHENONE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
4	2.07	0.89	43
5	2.28	0.56	24
6	0.72	0.68	95
8	0.15	0.07	48
9	0.11	0.09	82
14	0.48	0.12	25
15	0.95	0.27	28
18	0.66	0.30	46
20	1.30	0.29	22
21	1.88	0.85	45
22	1.67	0.53	31
23	2.38	0.68	29
26	1.48	0.66	45
B2	1.21	0.44	36

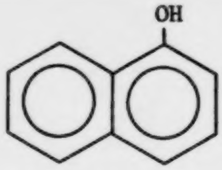
Comparison of samples 6 and 23 illustrates the organic carbon/clay interaction. Sample 6 gave an unexpectedly high Kp value (0.68) for its organic carbon content (0.72%). This apparently aberrant result can be partially explained by the high montmorillonite content (61%) of the sample sorbing acetophenone in excess of its organic carbon content. Sample 23, by contrast, had a similar Kp value (0.68) and yet was high in both montmorillonite (58%) and organic carbon (2.38%). Hence, for this sample the organic carbon appeared to mask the effect of the clay on sorbing acetophenone, and the relationship between Kp and organic carbon content remained valid.

Stevenson (23) reported that the relative contributions of organic and inorganic surfaces to adsorption depends on the extent to which the clay is coated with organic substances. He considered clay-humus and clay alone as two major types of adsorbing surfaces normally available to pesticides. Hence clays should exhibit their maximum influence on sorption of nonpolar compounds in the absence of adequate organic materials for coating the clays.

4.2. 1-NAPHTHOL

1-Naphthol (α-naphthol) was chosen to represent the aromatic alcohols or phenolic materials found in coal conversion waste streams (2). The physical properties of 1-naphthol are given in Table 4.4.

TABLE 4.4. PHYSICAL PROPERTIES OF 1-NAPHTHOL

Structure	
Molecular weight (Aldrich catalog, 1979-80)	144.17
Melting point (°C) (Aldrich catalog, 1979-80)	95-96
Boiling point (°C) (Aldrich catalog, 1979-80)	278-280
Heat of vaporization, ΔHv (cal/gmol) (CRC Handbook, 1975-76)	14,205.6

Water solubility was determined to be 866 μg/ml by the procedure given in Section 5.3. The octanol-water partition coefficient was determined to be 700 by the procedure given in Section 5.2.

Batch equilibrium sorption isotherms were determined using ^{14}C-labeled 1-naphthol (>99% pure) from Aldrich Chemical Co. Purity of the original solutions and the equilibrium isotherm solutions was verified by thin-layer chromatography. The sorption isotherms were determined in triplicate on a 1:10 soil to solution ratio (4.0 g soil/sediment and 40.0 ml solution) with initial concentrations ranging from 86 to 690 μg/ml. Samples were equilibrated in stainless steel centrifuge tubes (teflon-covered lids) in a temperature-controlled shaking water bath at 25°C for 24 hours. Initial and final aqueous phase concentrations of 1-naphthol were determined by liquid scintillation counting. The concentration of 1-naphthol sorbed by the soil/sediment phase was determined by difference. A ^{14}C mass balance was calculated to verify that there was no loss of the compound from the system. The ^{14}C mass balance was determined by converting the compound sorbed on the soil/sediment to $^{14}CO_2$ using a Packard Model 306 sample oxidizer. No significant loss of 1-naphthol was observed.

Soil thin-layer chromatography (TLC) was used to study the effect of solvent polarity on hydrophobic and nonhydrophobic sorption. Soil TLC plates were prepared by spreading a uniform layer of soil-water slurry 0.5 mm thick over 20x20-cm glass plates using the basic method of Helling and Turner (24). The plates were dried in a desiccated chamber and spotted with ^{14}C-labeled 1-naphthol using micropipette capillary tubes. Plates were developed in a chromatographic tank with the appropriate solvent and set with X-ray film in a darkroom. Rf values were determined by visual measurement of the developed film and verified by scraping and counting 1-cm segments from the developed plates in liquid scintillation vials containing 10 ml Aquasol (New England Nuclear).

The results of the sorption experiments with 1-naphthol are given in Tables 4.5 and 4.6. The isotherms were well represented by the Freundlich equation:

$$Cs = Kd \cdot Cw^{1/n} \qquad (4\text{-}3)$$

where Cs is the amount of compound sorbed by the soil or sediment in μmoles/g, Cw is the equilibrium solution concentration in μmoles/ml, and Kd and 1/n are constants. The 1/n values ranged from 0.222 to 0.642, while Kd values varied from 2.60 to 30.23. Representative isotherms are given in Figure 4.2. The isotherms were non-linear, as expected from their 1/n values.

Ten of the sixteen samples produced Koc values (Table 4.6) which were in good agreement with the Koc value (432) calculated from the octanol-water partition coefficient (700) of 1-naphthol. [N.B. The bulk of the present investigation involved 14 soil/sediment samples. Two additional samples, #13 and #B1, not referred to elsewhere in this report, were included in the 1-naphthol sorption isotherm determinations.] The remaining six samples gave Koc values that were much larger than the predicted value. This is further illustrated in Figure 4.3 which shows the relationship between Kd and the organic carbon content of the soils/sediments. The Kd values of ten samples were highly correlated ($r^2 = 0.876$) with organic carbon content, whereas the Kd values of the other six samples were not. The slope of the line in Figure 4.3 is equivalent to Koc and gave a value of 522 which is in good agreement with the predicted value.

The justification for excluding the six samples with high Koc values can be seen in Figure 4.4. This figure presents Koc as a function of the organic carbon to montmorillonite ratio of the soil or sediment. For 1-naphthol, there appeared to be two distinct families of data. One family of ten samples formed a line that was basically parallel to the %OC/%Mont axis and hence was independent of that variable. Those were the same soils and sediments whose Koc values converged on the predicted value and thus appeared to hydrophobically sorb 1-naphthol. The other six samples produced a line that appeared to be a function of the organic carbon to montmorillonite ratio. The data suggest that clay may sorb 1-naphthol in sediments with low to medium organic carbon contents, but may not be a major factor controlling sorption in soils or sediments with high organic carbon contents. Comparison of samples 23 and 26 which have high montmorillonite contents, but in combination with high organic carbon contents, with the six samples that gave high Koc values

TABLE 4.5. 1-NAPHTHOL SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (μmol/ml)	Cs[c] (μmol/g)	Sample	Cw (μmol/ml)	Cs (μmol/g)	Sample	Cw (μmol/ml)	Cs (μmol/g)
B2	0.06	5.40	4	0.03	5.72	5	0.21	3.95
	0.37	8.32		0.13	10.65		0.57	6.33
	1.20	11.93		0.58	18.16		1.45	9.55
	1.95	16.43		1.33	22.59		2.32	12.83
	2.90	18.82		2.00	27.82		3.17	16.89
6	0.010	5.88	8	0.44	1.55	9	0.01	5.84
	0.023	11.73		0.94	2.60		0.04	11.52
	0.234	21.59		1.99	3.99		0.62	17.74
	0.875	27.15		3.10	4.91		1.31	22.75
	1.52	32.62		4.15	6.38		2.38	24.04
14	0.24	1.32	15	0.002	2.91	18	0.05	5.56
	0.56	1.89		0.009	5.79		0.22	9.83
	1.18	3.18		0.038	11.29		1.00	14.06
	1.86	3.92		0.221	15.34		1.92	16.49
	2.53	4.75		0.430	19.21		2.98	18.31
20	0.004	2.90	21	0.19	3.73	22	0.23	3.71
	0.010	5.78		0.58	6.15		0.60	5.97
	0.104	10.71		1.41	9.87		1.43	9.66
	0.264	14.99		2.29	13.03		2.34	12.45
	0.617	17.35		3.26	15.28		2.59	21.94
23	0.08	5.25	26	0.15	4.56			
	0.32	8.81		0.49	7.10			
	0.92	14.88		1.29	11.04			
	1.96	16.45		2.07	15.20			
	2.68	21.26		3.12	16.62			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

TABLE 4.6. FREUNDLICH SORPTION CONSTANTS, r^2 VALUES AND Koc VALUES FOR THE SORPTION OF 1-NAPHTHOL BY SOILS AND SEDIMENTS

Sample	K (molar)	1/n(molar)	r^2	Koc
4	15.99	0.441	0.980	772
5	8.17	0.550	0.992	358
6	30.23	0.310	0.941	4,198
8	2.60	0.609	0.996	1,733
9	17.18	0.222	0.983	15,618
13	9.96	0.357	0.985	328
14	2.81	0.563	0.991	585
15	25.65	0.318	0.935	2,700
18	13.87	0.283	0.997	2,102
20	21.39	0.313	0.905	1,645
21	8.40	0.501	1.000	447
22	8.79	0.642	0.923	526
23	14.01	0.387	0.984	589
26	10.23	0.442	0.992	691
B1	8.15	0.549	0.979	905
B2	9.96	0.357	0.985	823

illustrates the interaction of clay and humus. The higher organic carbon contents of samples 23 and 26 probably masked the effect of the clay, lowering the amount of sorption to a level controlled by the organic carbon contents of the samples. Shin (25) reported an increase in the sorption of DDT with partial removal of soil organic matter. Stevenson (23) reported that the relative contribution of organic and inorganic surfaces to sorption depends on the extent to which the clay is coated with organic substances. He considered humus-clay and clay alone as two major types of sorbing surfaces normally available to organic sorbates.

In earlier work with the same sediment samples used in this study, acetophenone was shown to be hydrophobically sorbed by all but two of the samples, 6 and 9. The degree of departure of predicted and measured Koc values for acetophenone was much less than found with the six samples in the 1-naphthol experiments. Hydrophobic sorption was implied when there was a high degree of correlation between a compound's Kow value and sorption expressed on an organic carbon basis (Koc). The 1-naphthol and acetophenone

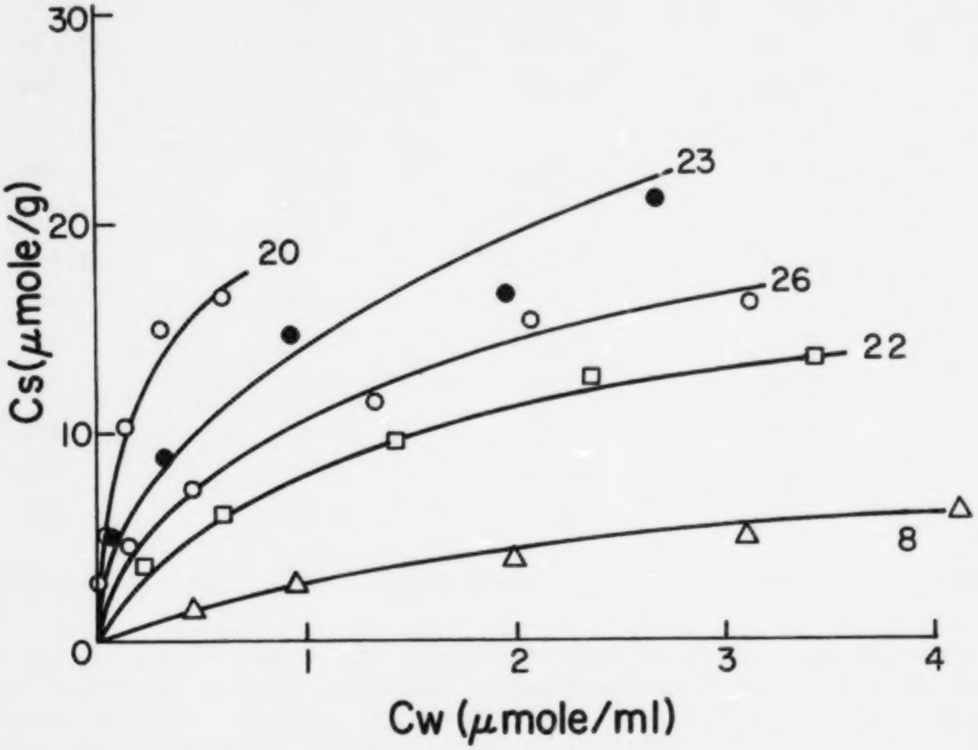


FIGURE 4.2. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 1-NAPHTHOL BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

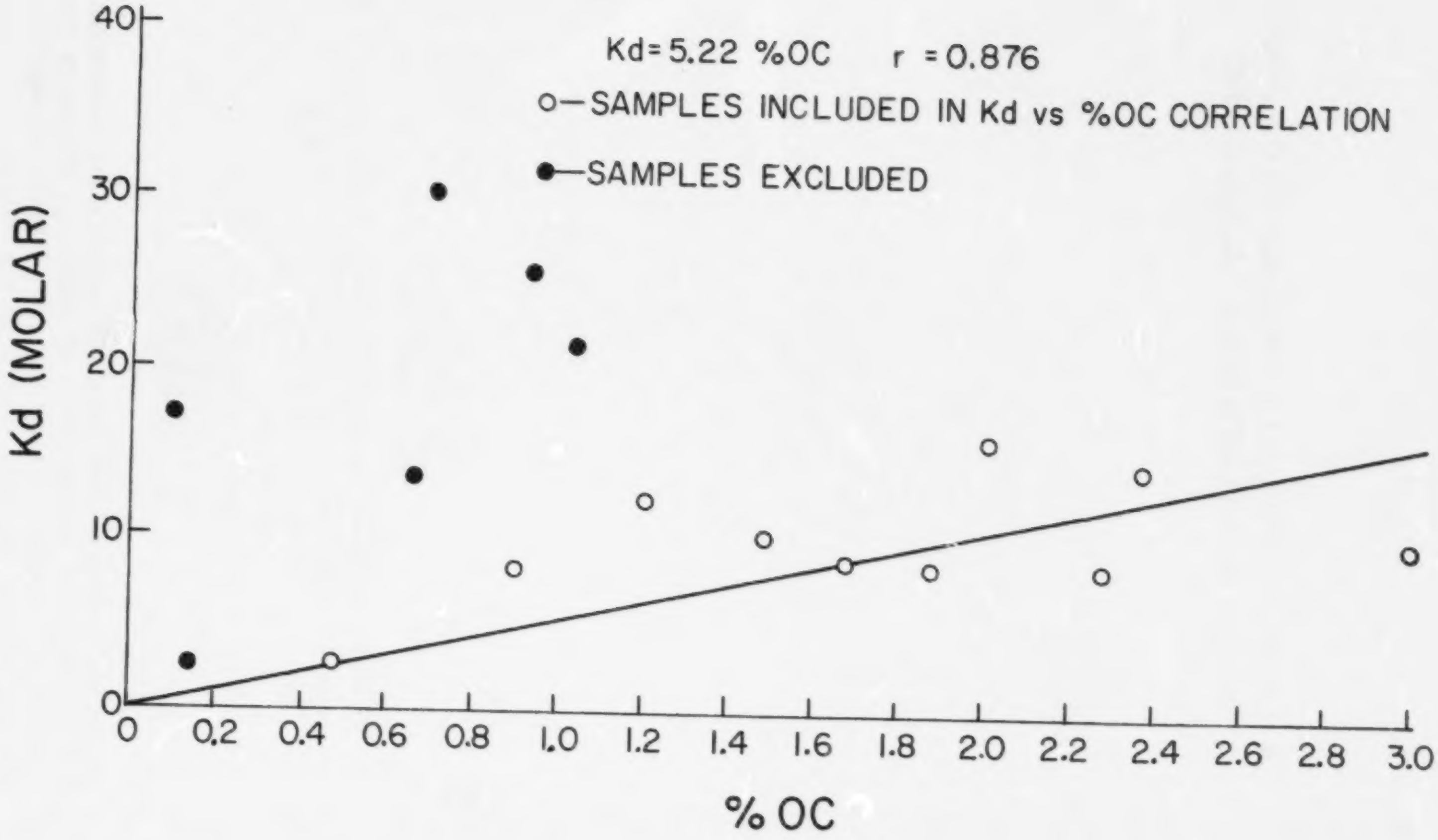


FIGURE 4.3. RELATIONSHIP BETWEEN MOLAR Kd (FOR THE SORPTION OF 1-NAPHTHOL) AND %OC FOR TEN SOIL AND SEDIMENT SAMPLES (○) SHOWING HIGH CORRELATION BETWEEN THE TWO PARAMETERS AND FOR SIX SAMPLES (●) THAT GAVE HIGH Koc VALUES

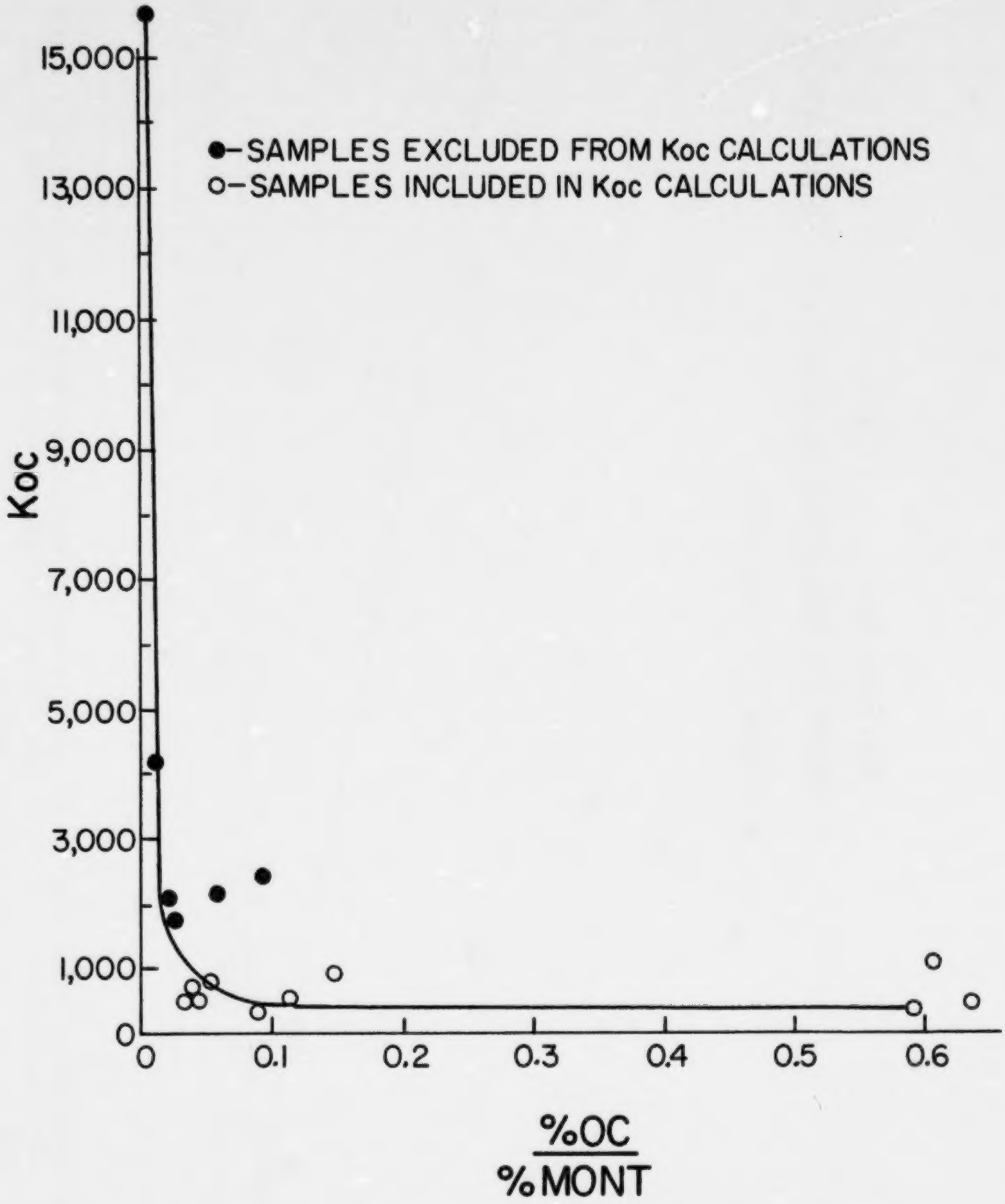


FIGURE 4.4. RELATIONSHIP BETWEEN Koc (FOR THE SORPTION OF 1-NAPHTHOL) AND THE %OC/MONTMORILLONITE RATIO OF SOILS AND SEDIMENTS FOR TEN SAMPLES (○) SHOWING HIGH CORRELATION BETWEEN Kd AND %OC AND FOR SIX SAMPLES (●) THAT GAVE HIGH Koc VALUES

data suggest that there is a lower limit (Kow value) where the correlation between Kow and Koc may not hold. The lower limit is not strictly a function of the compound's water solubility or its octanol-water partition coefficient, but is also a function of soil or sediment properties. Acetophenone has a water solubility of 5440 µg/ml and a Kow of 38.6 while 1-naphthol has a water solubility of 866 µg/ml and a Kow of 700. Despite the more polar nature of acetophenone in aqueous solutions, acetophenone appears to be hydrophobically sorbed by soils and sediments that do not hydrophobically sorb 1-naphthol. For 1-naphthol the Koc-Kow relationship may or may not hold for samples with organic carbon to montmorillonite ratios below 0.10; for acetophenone the relationship appears valid until a ratio of 0.015 or less is reached.

The role of the solute-solvent interaction in hydrophobic sorption is illustrated by a soil thin-layer chromatographic (24,26) study of 1-naphthol, dicamba (3,6-dichloro-2-methoxybenzoic acid) and 3-methylcholanthrene in different solvent systems (Figure 4.5). In the pure water system 1-naphthol and 3-methylcholanthrene were strongly sorbed and hence showed little or no movement, while dicamba which is a more polar and hence more water-soluble compound had an R_f value close to 1.0. Increasing the percentage of ethanol in the mobile phase resulted in higher R_f values for 1-naphthol and 3-methylcholanthrene and decreased movement or lower R_f values for dicamba. As the percentage of ethanol increased, the mobile phase became a continually better solvent for 1-naphthol and 3-methylcholanthrene, and hence a stronger and stronger solute-solvent interaction occurred resulting in decreased sorption. The effect of the composition of the mobile phase on dicamba, a polar material, was the opposite, as expected. As the percentage of ethanol increased, the mobile phase became less polar and hence a poorer solvent for dicamba. Sorption of dicamba increased and the R_f value dropped to less than 0.15 as the solute-solvent interaction weakened.

The sorption of 1-naphthol on ten of the sixteen samples appeared to be an example of hydrophobic sorption. Sorption of this type is the result of a weak solute-solvent interaction and the subsequent sorption of the compound by humic materials. Factors that increase the affinity of the solute for the solvent result in decreased sorption and increased mobility of the solute.

For compounds such as 1-naphthol and acetophenone the degree and type of sorption appears to be both a function of the water solubility or Kow value of the compound and a function of soil or sediment properties. One can speculate that as the water solubilities of compounds decrease, a point is reached where only hydrophobic sorption functions and sorption can be accurately predicted from Kow values. For compounds of higher water solubility they may be completely, partially or not at all hydrophobically sorbed.

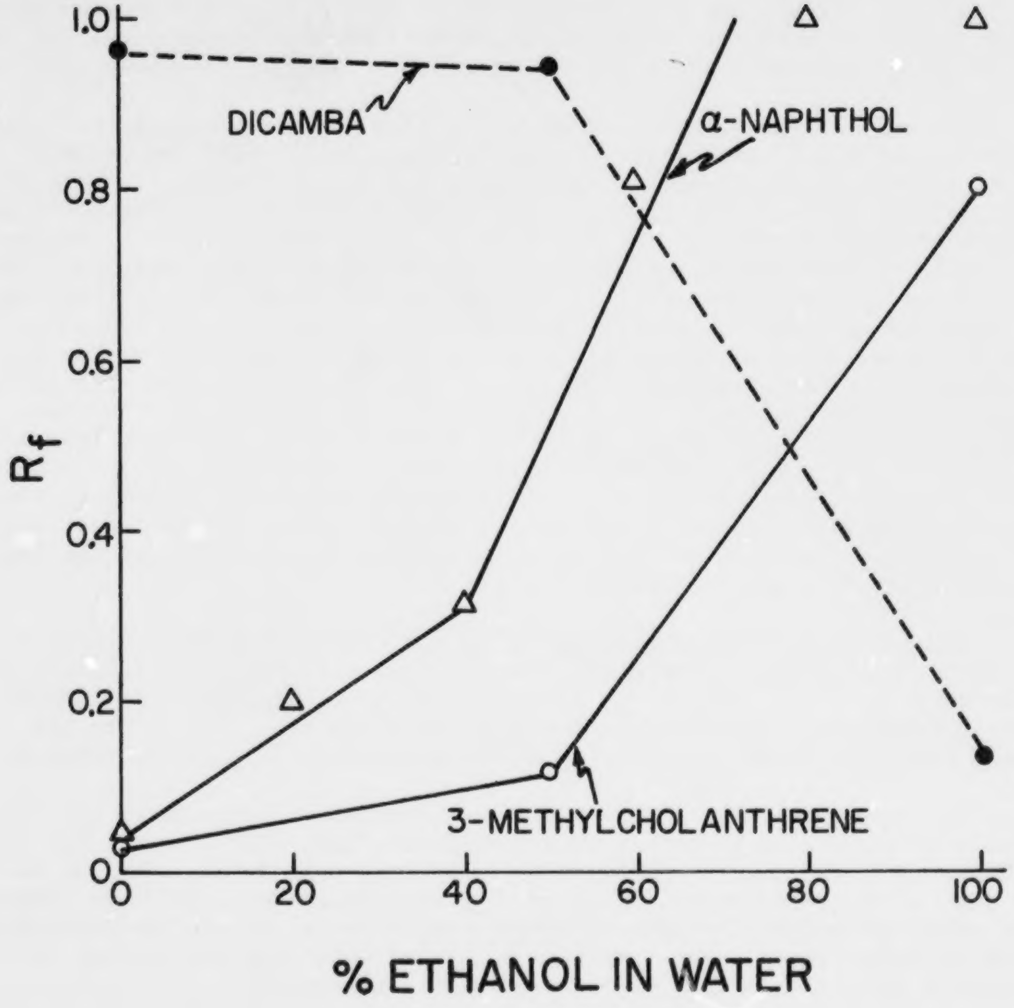
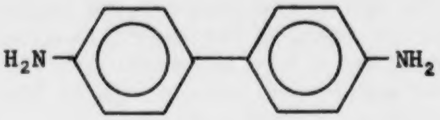


FIGURE 4.5. EFFECT OF VARYING THE ETHANOL:WATER RATIO IN THE SOLVENT SYSTEM ON SOIL TLC R_f VALUES FOR DICAMBA, α-NAPHTHOL AND 3-METHYLCHOLANTHRENE

4.3. BENZIDINE

Benzidine (4,4'-diaminobiphenyl) and compounds of similar chemical and physiological properties are potential waste products of coal conversion plants (2) and other industrial activities. The introduction of benzidine, an aromatic amine, into the environment is reason for concern since benzidine has been identified as a potent carcinogen (27,28,29,30). The physical properties of benzidine are given in Table 4.7.

TABLE 4.7. PHYSICAL PROPERTIES OF BENZIDINE

Structure	
Molecular weight (CRC Handbook, 1975-76)	184.24
Melting point (°C) (CRC Handbook, 1975-76)	125
Boiling point (°C) (CRC Handbook, 1975-76)	400
pKb_1 (Korenman and Nikolaev (31))	4.3
pKb_2 (Korenman and Nikolaev (31))	3.3

The interaction of benzidine with clays, especially montmorillonite, has been extensively studied as benzidine forms a blue-colored complex with the clay upon sorption. The benzidine-clay complex is the result of the reversible oxidations of the benzidine by ferric iron or other electron donors with stabilization of the product by sorption to the clay. In the absence of clay or other suitable sorbents benzidine is irreversibly oxidized to a brown degradation product. The blue color of the benzidine-clay complex arises from the semiquinoidal radical cation of benzidine. A yellow quinoidal divalent cation is formed in acidic aqueous solutions of benzidine and clay. Benzidine may also form cations by protonation of the amino groups. The early research on benzidine-clay reactions has been reviewed by Solomon *et al.* (32) and Theng (33). Tennakoon *et al.* (34 , 35 , 36) discuss the proposed mechanism of benzidine-clay reactions.

Batch equilibrium sorption isotherms were performed using ^{14}C-labeled benzidine obtained from New England Nuclear. Unlabeled benzidine (RFR Corp., Hope, RI) was used to adjust the activity of the labeled compound. A stock aqueous solution of benzidine containing 270 µg/ml and 3900 dpm/ml was prepared using ultrapure water. The purity of the stock solution was determined to be at least 98% by thin-layer chromatography. The sorption isotherms were determined in triplicate using 4g:40 ml soil:solution ratio. Initial concentrations ranged from 67 to 270 µg/ml. A few samples exhibited very strong sorption resulting in extremely low levels of benzidine left in solution. For these samples, isotherms were determined by varying the amount of soil or sediment from 0.25 g to 0.40 g and keeping the initial benzidine concentration constant at 270 µg/ml (40 ml).

The samples were equilibrated in stainless steel centrifuge tubes at 25°C for 20 hours in a temperature-controlled shaking water bath. After equilibration the phases were separated by centrifugation and the aqueous phase was sampled for scintillation counting. The ^{14}C activity was determined using a Packard model 3330 liquid scintillation spectrometer. The amount sorbed was calculated as the difference between initial and equilibrium concentrations.

The extent of benzidine degradation in the equilibrium solutions was determined by gas chromatography. A Packard model 417 gas chromatograph with a flame ionization detector and a 2-m SE-30 column with a flow rate of 16ml/min N_2 carrier gas was used. The system was standardized using known solutions of benzidine and diphenylazine, a suspected degradation product. No extraneous peaks were observed for the equilibrium isotherm solutions.

The sorption of benzidine by soils and sediments produced isotherms which were well represented by the Freundlich equation:

$$Cs = Kd \cdot Cw^{1/n} \qquad (4\text{-}3)$$

where Cs is the concentration of benzidine in nmoles/g of soil or sediment, Cw is the equilibrium solution concentration in nmoles/ml and Kd and 1/n are constants. Representative isotherms are shown in Figure 4.6 and sorption constants are given Table 4.8. Average values for the sorption data are given in Table 4.9. Attempts to fit the data to the Langmuir equation gave poor fits both visually and statistically.

Neither Freundlich constant was highly correlated with soil or sediment properties. This was probably due to the fact that variation between isotherms for different soils and sediments was expressed in two constants, Kd and 1/n. Small changes in the exponential constant 1/n can result in large changes in the Kd values and hence poor correlation with soil or sediment properties. To overcome this difficulty the sorption data were fit to a Freundlich equation (Kd_2) where the exponential constant (1/n) had a value of 0.5. The mean of the 1/n values in Table 4.8 was 0.515.

$$Cs = Kd_2 \cdot Cw^{0.5} \qquad (4\text{-}4)$$

The resulting Kd_2 values and correlation coefficients for the fit of the data are given in Table 4.10. The Kd_2 values were highly correlated ($r^2 = 0.92$) with hydrogen ion activities as calculated from pH measurements.

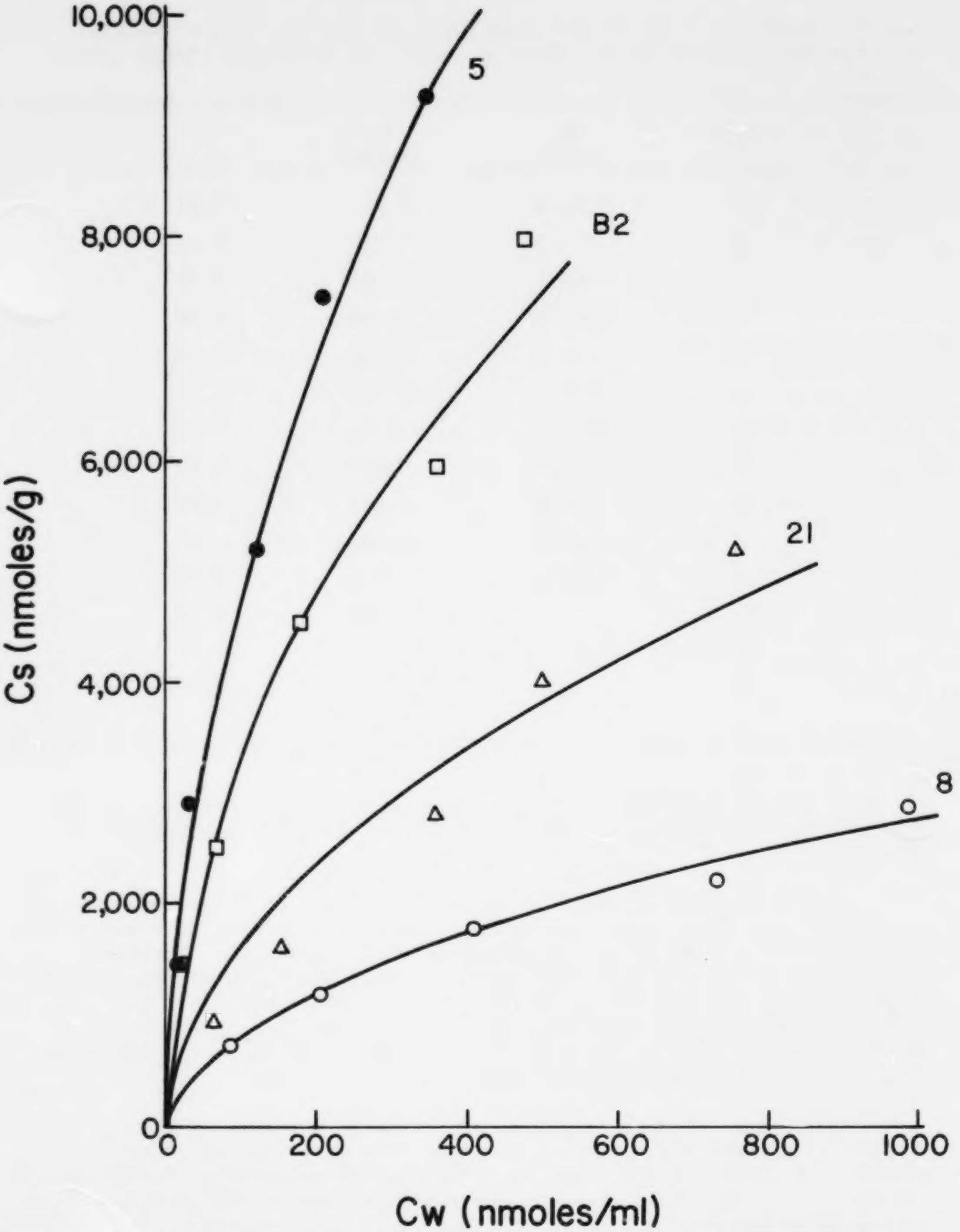


FIGURE 4.6. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF BENZIDINE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.8. FREUNDLICH CONSTANTS (Kd and 1/n) AND r^2 VALUES FOR THE SORPTION OF BENZIDINE BY SOILS AND SEDIMENTS (MOLAR BASIS)

Sample	Kd (molar)	1/n (molar)	r^2
B2	500.4	0.423	0.91
4	570.5	0.513	0.96
5	589.4	0.468	0.97
6	1657.8	0.568	0.94
8	86.2	0.496	0.83
9	551.7	0.372	0.94
14	3941.3	0.664	0.93
15	1705.4	0.266	0.93
18	564.6	0.413	0.96
20	2332.9	0.426	0.91
21	49.6	0.694	0.97
22	73.9	0.640	0.95
23	1072.7	0.569	0.96
26	108.2	0.656	0.89

The data suggest that the pH of the system controls the sorption of the benzidine by controlling the amount of benzidine in the ionized form in solution.

The dependence of sorption on pH can further be illustrated by the results of experiments where sorption of benzidine by samples 6 and 14 was determined before and after adjustment of pH (Figure 4.7). For these experiments pH was adjusted with either concentrated NaOH or HCl, and the resultant sorption and pH values were measured after equilibration under the same sorption isotherm conditions described above. Sorption increased as pH decreased, that is, as a greater percentage of the total benzidine occurred as a charged (cationic) species.

Benzidine, as already noted, can exist in solution as both an ionized (cationic) species and a neutral species. The distribution of aqueous benzidine between the two forms is a function of solution pH. Both species are subject to sorption, although the cationic form should be sorbed to a much greater extent.

Karickhoff *et al.* (15) and Khan *et al.* (16) established a relationship between the octanol-water partition coefficient (Kow) of a

TABLE 4.9. BENZIDINE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (nmol/ml)	Cs[c] (nmol/g)	Sample	Cw (nmol/ml)	Cs (nmol/g)	Sample	Cw (nmol/ml)	Cs (nmol/g)
B2	17	1419	4	8	1504	5	8	1509
	64	2533		20	2976		27	2901
	187	4476		69	5662		138	4966
	354	5984		166	7866		215	7371
	467	8026		262	10084		360	9100
6	1	1577	8	87	718	9	8	1509
	4	3140		210	1080		47	2705
	11	6239		454	1793		218	4169
	25	9272		734	2186		396	5564
	47	12233		995	2746		620	6502
14	0.11	1589	15	0.63	1579	18	14	1448
	1.67	3159		6	3110		39	2787
	2.75	6323		78	5573		159	4764
	3.88	9487		215	7377		340	6124
	5.17	12649		412	8576		502	7680
20	1.42	1573	21	69	896	22	69	899
	1.9	3153		149	1683		141	1764
	5	6296		355	2801		364	2698
	25	9276		539	4136		559	3938
	111	11594		771	4987		754	5124
23	1.6	1569	26	41	1178			
	8	3099		102	2155			
	18	6171		261	3734			
	53	8994		410	5428			
	80	11902		545	7246			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

TABLE 4.10. MODIFIED FREUNDLICH PARTITION CONSTANTS (1/n = 0.5) FOR THE SORPTION OF BENZIDINE (Kd_2) AND IONIZED BENZIDINE (Kd_3) BY SOILS AND SEDIMENTS (MOLAR BASIS)

Sample	Kd_2 (molar)	r^2	Kd_3 (molar)	r^2
B2	339.1	0.99	3,552	0.99
4	609.8	0.99	33,542	0.99
5	498.0	0.99	18,206	0.99
6	2851.8	0.98	165,780	0.98
8	85.9	0.98	8,693	0.98
9	259.8	0.98	27,138	0.98
14	8037.2	0.98	13,063	0.98
15	473.8	0.95	26,132	0.95
18	344.5	0.99	18,352	0.99
20	1558.8	0.98	6,347	0.98
21	167.6	0.98	7,048	0.98
22	177.4	0.98	7,116	0.98
23	1790.3	0.98	28,208	0.98
26	276.7	0.96	14,335	0.96

nonpolar neutral compound and the linear partition coefficient for the sorption of the compound by soils and sediments:

$$\log (Kp/OC) = \log Kow - 0.21 \qquad (4\text{-}5)$$

where Kp is the linear sorption or partition coefficient of a compound on a particular soil or sediment and OC is the organic carbon content of the soil or sediment expressed on a fractional basis.

The relationship expressed in equation 4-5 has been shown to apply to unionized hydrophobic organic compounds and is attributed to the hydrophobic or nonpolar bonding (14) of the compound to the soil or sediment organic matter (15,16).

If the assumption is made that neutral benzidine will bind via hydrophobic bonding to soil organic matter, then equation 4-5 can be used to calculate the individual Kp values for the sorption of neutral benzidine by the soils and sediments. Calculations were based on the soil and sediments' organic carbon contents and the Kow (46.0) of benzidine. Three equations may

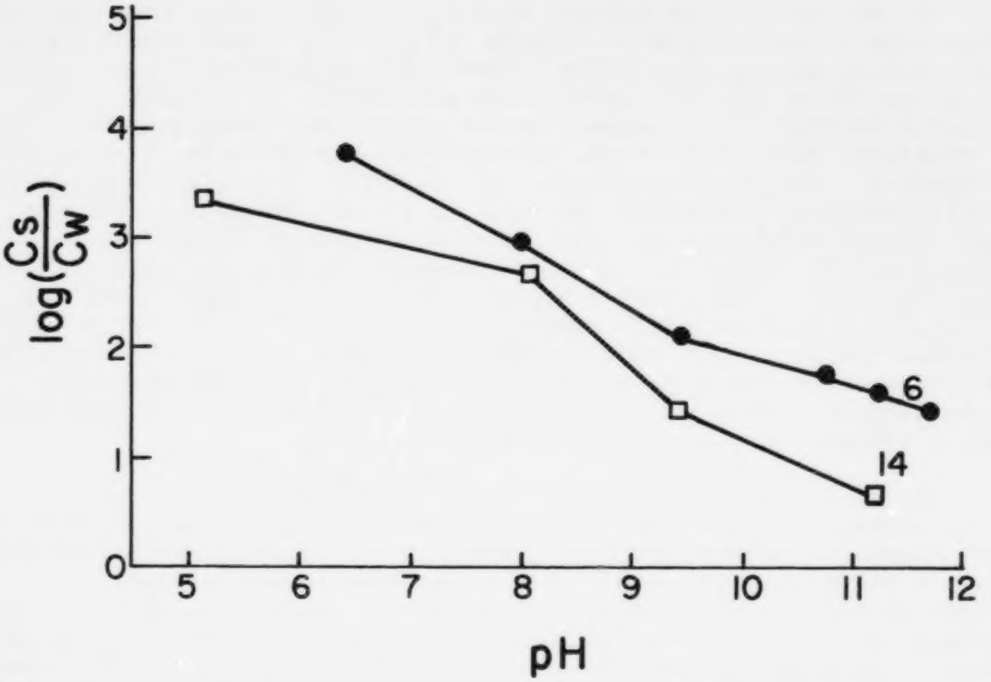


FIGURE 4.7. EFFECT OF pH ON THE SORPTION OF BENZIDINE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

then be written to model the sorption of benzidine by soils and sediments:

$$\text{bzn(sorbed)} = \text{Kp} \cdot \text{bzn(aq)} \tag{4-6}$$

$$\text{bzn (aq)} + 2\text{H}^{+} = \text{bzn H}_2^{2+}\text{(aq)} \quad K = \text{Kb}_1 \cdot \text{Kb}_2 \tag{4-7}$$

$$\text{bzn H}_2^{2+}\text{(sorbed)} = \text{Kd} \cdot \text{bzn H}_2^{2+}\text{(aq)}^{0.5} \tag{4-8}$$

Using Kp values calculated from equation 4-5, H^+ activities calculated from measured pH values, and the total amount of benzidine added, equations 4-6, 4-7, and 4-8 can be solved to yield the Freundlich sorption constant Kd_3 ($1/n = 0.5$) for the sorption of the ionized benzidine by each soil or sediment (Table 4.10).

The Kd_3 values thus obtained were significantly correlated with the surface area of the soils and sediments ($r^2 = 0.72$). Addition of organic carbon content and the interaction between surface area and organic carbon to the the regression equation improved the correlation ($r^2 = 0.86$). The regression coefficient for organic carbon content was non-significant while the regression coefficient of the interaction was significant ($t = -2.379$) and negative. This suggests that organic materials coat clay particles and lower the sorption capacity of the soil for ionized benzidine. The clay-organic matter interaction is illustrated by comparing the Kd_3 values for samples 6 and 23. Both samples have comparable textures and clay mineralogy. Sample 23, however, has a higher organic carbon content which appears to mask the clay and consequently this sample sorbs substantially less of the ionized benzidine. The effect of surface area on benzidine sorption is illustrated in Figure 4.6. At any given pH, sample 6 which contains predominantly montmorillonite clays sorbs greater amounts of benzidine than sample 14 which contains predominantly kaolinite clays.

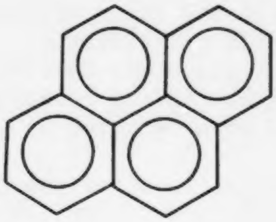
The sorption of benzidine by "whole" soils and sediments was controlled primarily by the concentration of the ionized species. Sorption was highly correlated with pH since pH controlled the ratio of neutral to ionized benzidine in the aqueous phase. When the isotherms were corrected for sorption of the neutral species, sorption of the ionized benzidine was highly correlated with surface area and negatively correlated with organic carbon content. The organic matter appeared to coat and hence mask ionized benzidine sorption sites. These experiments suggest that extrapolation of sorption data from studies involving only clay minerals to situations involving "whole" soils or sediments may produce erroneous results.

4.4 PYRENE

Pyrene, 3-methylcholanthrene, dibenz[*a,h*]anthracene and 7,12-dimethylbenz[*a*]anthracene were chosen as representatives of the polynuclear aromatic hydrocarbons. The compounds represent different configurations of four and five-ring structures. The factors affecting the sorption of these compounds are discussed in Section 4.7.

The physical properties of pyrene are given in Table 4.11.

TABLE 4.11. PHYSICAL PROPERTIES OF PYRENE

Structure	
Molecular weight (CRC Handbook, 1975-76)	202.26
Melting point (°C) (CRC Handbook, 1975-76)	156
Boiling point (°C) (CRC Handbook, 1975-76)	393
Density (CRC Handbook, 1975-76)	1.271

The octanol-water partition coefficient (Kow) of pyrene was determined over a range of aqueous concentrations using radiolabeled compound and the procedure outlined in Section 5.2. A Kow value of 124,000 was obtained for pyrene. The water solubility of pyrene was determined to be 0.135 μg/ml by the procedure described in Section 5.3.

Batch equilibrium sorption isotherms were determined using ^{3}H-labeled pyrene that had been tritiated by the method outlined in Section 5.1.3. The unlabeled pyrene used in the tritiation procedure was obtained from Aldrich Chemical Co. (>99% pure). The resulting generally-labeled ^{3}H-pyrene was purified by microdistillation followed by preparative thin-layer chromatography.

An aqueous solution was prepared by evaporating (under a stream of N_2 gas) an appropriate quantity of ^{3}H-labeled pyrene stock solution on the lower walls of a glass container, adding ultrapure water and stirring for 24 hours. The resulting solution was filtered through a 0.2μ Nuclepore filter to remove any undissolved particles and diluted with ultrapure water to the desired concentrations.

The sorption isotherms were determined in triplicate on a 1:10 soil to solution ratio, with initial pyrene concentrations ranging from 10 to 80 μg/ml (the upper initial concentration representing ∿59% of the maximum water solubility level). Isotherm suspensions were shaken in stainless steel centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours.

Initial and final aqueous phase concentrations of pyrene were determined by liquid scintillation counting. The amount of pyrene sorbed by the soil/sediment phase was determined from the difference between the initial and final aqueous phase concentrations. No degradation products were found in either phase when analyzed by the procedure described in Section 5.4.1.

The sorption of pyrene by the soils and sediments produced linear sorption isotherms over the entire range of concentrations studied. Typical isotherms are shown in Figure 4.8. Average Cw and Cs values for the sorption of pyrene by the soils and sediments are given in Table 4.12. The data gave good fits to the Freundlich sorption isotherm equation:

$$Cs = Kd \cdot Cw^{1/n} \qquad (4\text{-}3)$$

Kd values (Table 4.13) ranged from 79 to 1191; the 1/n values were all close to unity. The data gave equally good fits (Table 4.14) to the modified Freundlich equation where 1/n was forced to equal unity. Koc values calculated from the linear partition coefficients (Kp) and the respective organic carbon contents of the sediments and soils are also included in Table 4.14. Regression of Kp against the organic carbon contents of the sediments and soils produced a Koc value of 63,400 ($r^2 = 0.965$).

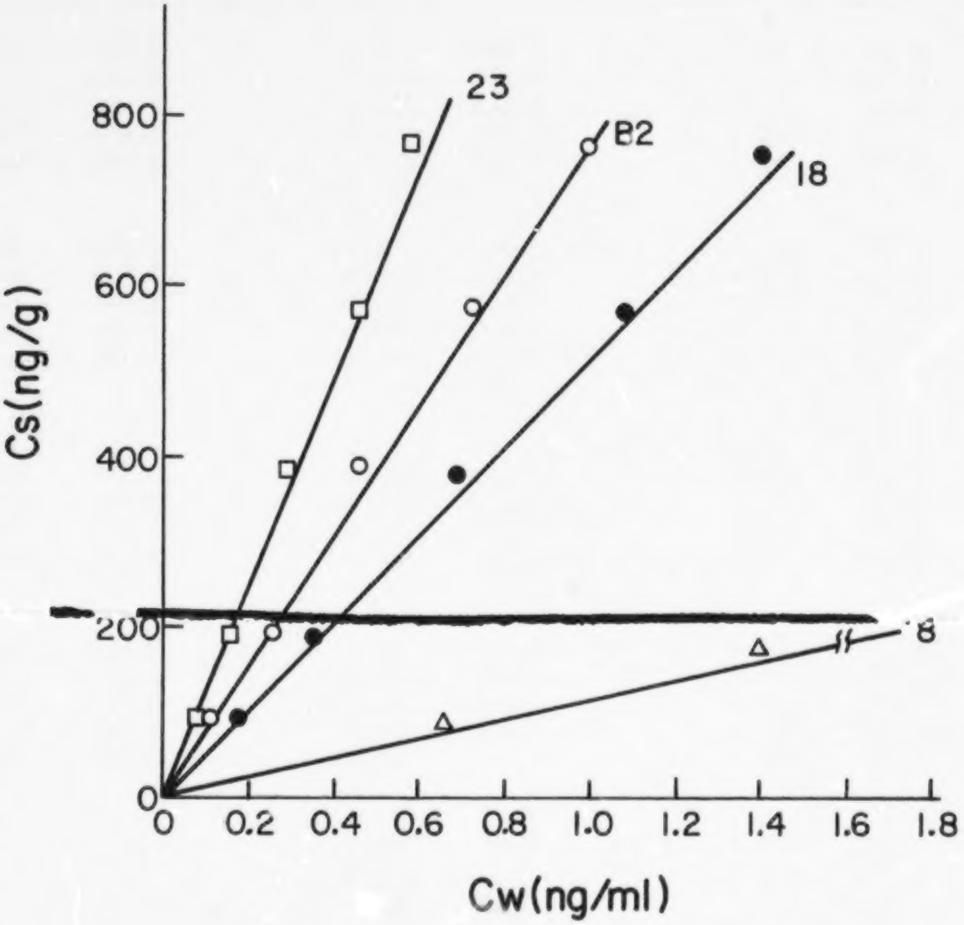


FIGURE 4.8. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF PYRENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.12. PYRENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.128	95.0	4	0.094	95.3	5	0.084	95.4
	0.245	190.1		0.179	190.7		0.163	190.9
	0.441	380.6		0.343	381.6		0.300	382.0
	0.722	570.3		0.491	572.6		0.444	573.1
	0.989	760.1		0.698	763.0		0.585	764.1
6	0.124	95.0	8	0.657	89.7	9	1.126	85.0
	0.263	189.9		1.421	178.3		2.429	168.2
	0.495	380.1		3.188	353.1		4.061	344.4
	0.754	570.0		5.145	526.1		7.128	506.2
	1.010	759.9		7.495	695.1		8.153	688.5
14	0.345	92.8	15	0.123	95.0	18	0.187	94.4
	0.688	185.6		0.243	190.1		0.364	188.9
	1.253	372.5		0.509	379.9		0.688	378.1
	2.184	555.7		0.747	570.0		1.076	566.7
	2.995	740.1		1.027	759.7		1.410	755.9
20	0.137	94.9	21	0.097	95.3	22	0.154	94.7
	0.257	189.9		0.197	190.5		0.271	189.8
	0.542	379.6		0.352	381.5		0.500	380.0
	0.813	569.4		0.531	572.2		0.740	570.1
	1.137	758.6		0.709	762.9		0.984	760.2
23	0.096	95.3	26	0.111	95.1			
	0.176	190.7		0.199	190.5			
	0.292	382.1		0.382	381.2			
	0.440	573.2		0.562	571.9			
	0.587	764.1		0.759	762.4			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

TABLE 4.13. FREUNDLICH SORPTION CONSTANTS AND CORRELATION COEFFICIENTS (K_d, 1/n and r^2) AND THE MODIFIED FREUNDLICH PARTITION CONSTANTS (K_p, 1/n = 1) FOR THE SORPTION OF PYRENE BY SOILS AND SEDIMENTS

Sample	Kd	1/n	r^2	Kp
B2	774	1.022	0.988	760
4	1098	1.020	0.995	1065
5	1191	1.041	0.981	1155
6	633	0.943	0.964	614
8	125	0.876	0.989	101
9	79	0.953	0.979	71
14	285	0.967	0.978	277
15	783	0.977	0.994	783
18	509	0.989	0.995	504
20	747	0.987	0.986	723
21	1159	1.053	0.990	1119
22	811	1.026	0.977	806
23	1130	1.063	0.942	1043
26	1023	1.044	0.994	994

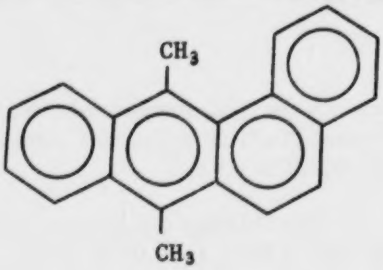
TABLE 4.14. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF PYRENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	760	63,991
4	2.07	1065	53,019
5	2.28	1155	52,250
6	0.72	614	87,847
8	0.15	101	83,333
9	0.11	71	71,818
14	0.48	277	59,271
15	0.95	783	82,453
18	0.66	504	77,182
20	1.30	723	57,469
21	1.88	1119	61,628
22	1.67	806	48,557
23	2.38	1043	47,487
26	1.48	994	69,108

4.5. 7,12-DIMETHYLBENZ[*a*]ANTHRACENE

7,12-Dimethylbenz[*a*]anthracene (9,10-dimethyl-1,2-benzanthracene, DMBA) was chosen as one of four compounds representing the polynuclear aromatic hydrocarbons. The physical properties of DMBA are given in Table 4.15.

TABLE 4.15. PHYSICAL PROPERTIES OF 7,12-DIMETHYLBENZ[*a*]ANTHRACENE

Structure	
Molecular weight (CRC Handbook, 1975-76)	256.35
Melting point (°C) (CRC Handbook, 1975-76)	122-123

The octanol-water partition coefficient of DMBA was determined over a range of aqueous concentrations using radiolabeled compound and the procedure described in Section 5.2. A Kow value of 953,000 was obtained. The water solubility of DMBA was determined to be 0.0244 μg/ml by the procedure given in Section 5.3.

Batch equilibrium isotherms were determined using ^{14}C-labeled DMBA obtained from New England Nuclear. Purity of the radiolabeled compound was verified by thin-layer chromatography. Appropriate amounts of DMBA were plated from acetone solution onto the walls of stainless steel centrifuge tubes using the procedure of Karickhoff *et al.* (15) for hydrophobic compounds. These amounts represented the initial aqueous phase concentrations (2.54 to 12.27 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 4 g:40 ml soil to solution ratio. The suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 20 hours. The phases were separated by centrifugation.

Initial and final aqueous phase concentrations of DMBA were determined by liquid scintillation counting. The amount of DMBA sorbed by the soil/sediment phase was calculated from the difference between initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure outlined in Section 5.4.1.

The sorption of DMBA by the soils and sediments produced linear isotherms over the entire concentration range studied. Representative isotherms are shown in Figure 4.9. Average values for the sorption isotherm data for each soil and sediment are given in Table 4.16. The sorption isotherms were described by the following equation:

$$Cs = Kp \cdot Cw \qquad (4\text{-}1)$$

where Cs is the amount of DMBA sorbed by the soil or sediment in ng/g, Cw is the equilibrium solution concentration in ng/ml, and Kp is the linear partition coefficient.

The linear partition coefficients and Koc values for the sorption of DMBA are given in Table 4.17. The Kp values varied from a low of 562 to a high of 6777. Regression of Kp against the organic carbon content of the soils and sediments produced a Koc value of 225,308 ($r^2 = 0.908$). The sorption of DMBA was not highly correlated with other soil or sediment properties such as pH, CEC, clay content or mineralogy.

The sorption of DMBA is discussed in Section 4.7 along with sorption of the other three polynuclear aromatic hydrocarbons studied.

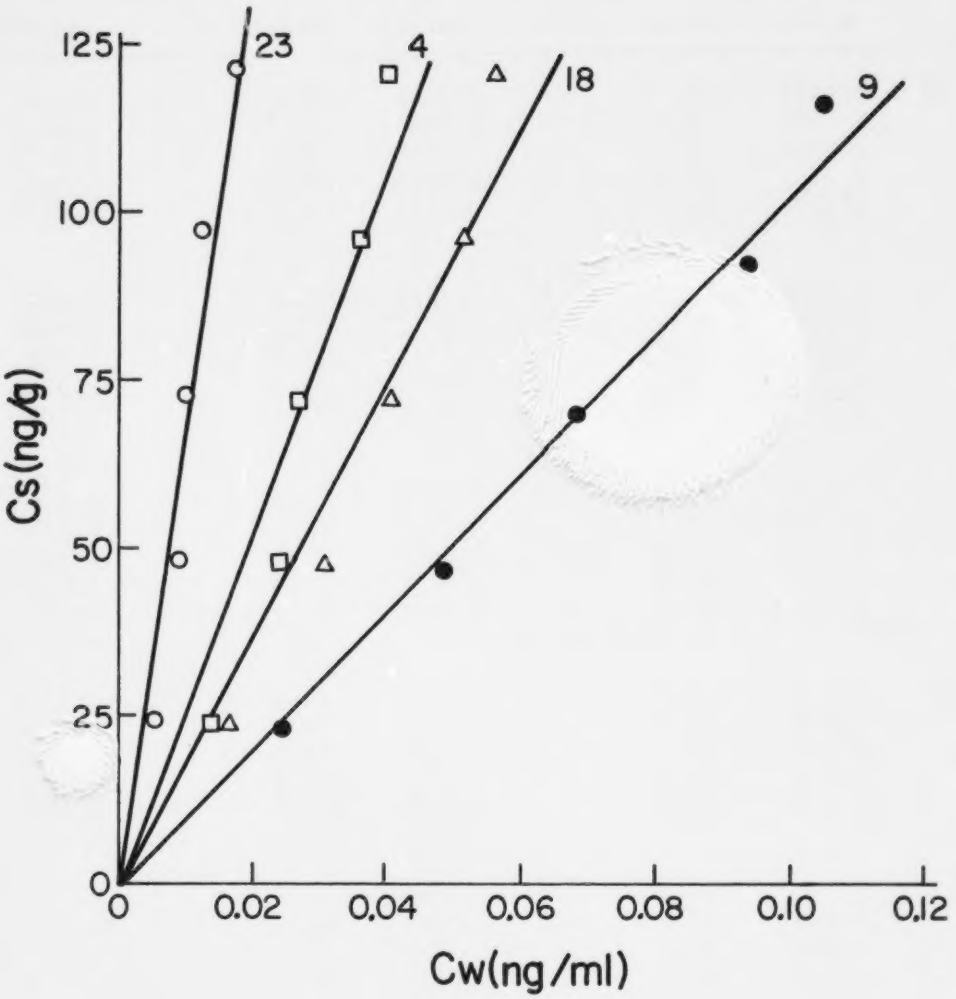


FIGURE 4.9. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 7,12-DIMETHYLBENZ[*a*]ANTHRACENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.16. 7,12-DIMETHYLBENZ[*a*]ANTHRACENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.0164	24.0	4	0.0145	24.0	5	0.0077	24.2
	0.0225	48.4		0.0242	48.2		0.0122	48.6
	0.0301	72.7		0.0270	72.7		0.0141	73.1
	0.0411	97.0		0.0366	96.9		0.0182	97.4
	0.0459	121.4		0.0403	121.4		0.0206	121.9
6	0.0298	23.4	8	0.0473	22.6	9	0.0246	23.0
	0.0414	47.6		0.0770	45.9		0.0485	46.0
	0.0604	71.4		0.1217	68.6		0.0684	69.3
	0.0656	95.8		0.1499	92.0		0.0942	92.2
	0.0785	119.8		0.9776	115.4		0.1055	116.0
14	0.0493	23.2	15	0.0089	24.3	18	0.0167	23.9
	0.1016	46.2		0.0140	48.7		0.0310	47.9
	0.1229	70.2		0.0194	73.1		0.0409	72.2
	0.1707	93.4		0.0258	97.5		0.0518	96.3
	0.1922	117.3		0.0313	121.9		0.0562	120.7
20	0.0169	24.0	21	0.0055	24.3	22	0.0117	24.1
	0.0346	47.8		0.0095	48.7		0.0227	48.2
	0.0429	72.1		0.0119	73.2		0.0282	72.5
	0.0641	95.9		0.0170	97.5		0.0342	96.9
	0.0673	120.3		0.0222	121.8		0.0427	121.1
23	0.0055	24.2	26	0.0089	24.3			
	0.0092	48.6		0.0159	48.6			
	0.0107	73.0		0.0186	73.1			
	0.0129	97.5		0.0255	97.4			
	0.0172	121.7		0.0313	121.8			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

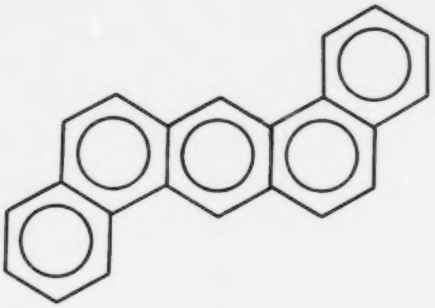
TABLE 4.17. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF 7,12-DIMETHYLBENZ[*a*]ANTHRACENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	2371	195,998
4	2.07	2646	127,812
5	2.28	5210	228,499
6	0.72	1346	186,986
8	0.15	611	407,496
9	0.11	1028	934,225
14	0.48	562	117,161
15	0.95	3742	393,907
18	0.66	1895	287,196
20	1.30	1617	124,347
21	1.88	5576	296,580
22	1.67	2679	160,391
23	2.38	6777	284,743
26	1.48	3740	252,735

4.6. DIBENZ[*a,h*]ANTHRACENE

Dibenz[*a,h*]anthracene (1,2,5,6-dibenzanthracene) was chosen as a representative polynuclear aromatic hydrocarbon containing five aromatic rings. Dibenzanthracene is the least water-soluble and hence most hydrophobic of the compounds used in this study. The physical properties of dibenz[*a,h*]anthracene are given in Table 4.18.

TABLE 4.18. PHYSICAL PROPERTIES OF DIBENZ[*a,h*]ANTHRACENE

Structure	
Molecular weight (CRC Handbook, 1975-76)	278.36
Melting point (°C) (CRC Handbook, 1975-76)	269-270
Boiling point (°C) (Aldrich catalog, 1979-80)	524

The octanol-water partition coefficient for dibenzanthracene was determined over a range of aqueous concentrations with radiolabeled compound using the procedure described in Section 5.2. A Kow value of 3,170,000 was obtained. The water solubility of dibenzanthracene was determined to be 0.00249 µg/ml by the procedure outlined in Section 5.3.

Batch equilibrium isotherms were determined using ^{3}H-labeled dibenzanthracene obtained from New England Nuclear. Purity of the radiolabeled compound was verified by thin-layer chromatography. Appropriate amounts of dibenzanthracene were plated from acetone solution onto the walls of the stainless steel centrifuge tubes using the procedure of Karickhoff *et al.* (15) for hydrophobic compounds. These amounts represented the initial aqueous phase concentrations (0.97 to 7.28 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 2 g:40 ml soil to solution ratio. The suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours. The phases were separated by centrifugation.

Initial and final aqueous phase concentrations of dibenzanthracene were determined by liquid scintillation counting. The amount of dibenzanthracene sorbed by the soil/sediment phase was calculated from the difference between initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure outlined in Section 5.4.1.

Sorption of dibenzanthracene by the sediments and soils produced linear isotherms over the entire range of concentrations studied. Representative isotherms are shown in Figure 4.10.

Average values for individual isotherms are given in Table 4.19. The sorption isotherms were described by the following equation:

$$Cs = Kp \cdot Cw \qquad (4\text{-}1)$$

where Cs is the amount of dibenzanthracene sorbed by the soil or sediment, Cw is the equilibrium solution concentration, and Kp is the linear partition coefficient.

The linear partition coefficients and Koc values are given in Table 4.20. The Kp values ranged from 1759 for low organic carbon-containing sediments to 55,697 for high organic carbon-containing sediments. Sorption of dibenzanthracene was highly correlated with soil organic carbon content but fairly independent of all other soil properties. Regression of Kp against soil or sediment organic carbon content gave a Koc value of 1,668,800 ($r^2 = 0.783$).

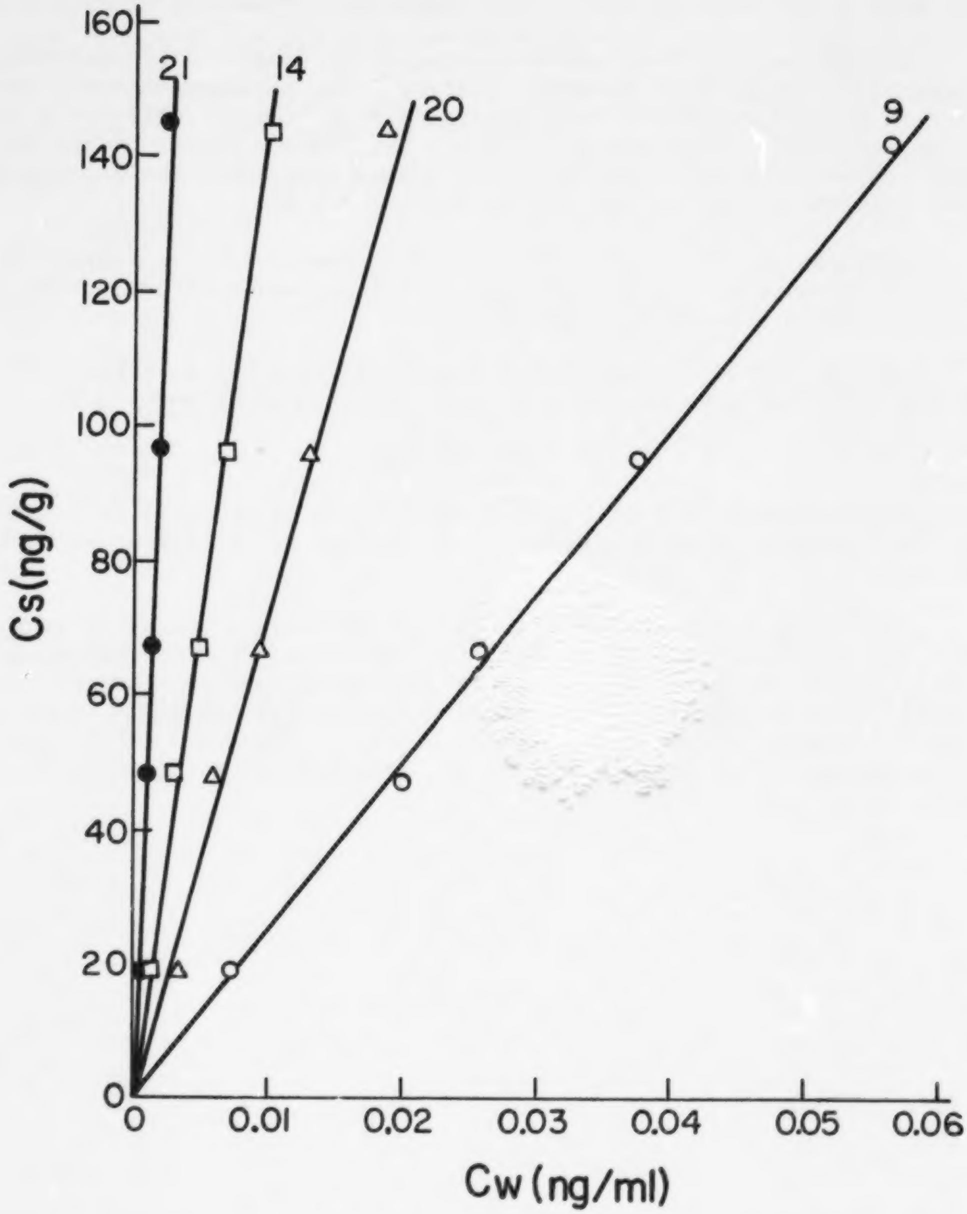


FIGURE 4.10. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF DIBENZ[*a*,*h*]-ANTHRACENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.19. DIBENZ[*a,h*]ANTHRACENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.0016	19.3	4	0.0010	19.3	5	0.0018	19.3
	0.0024	48.4		0.0021	48.4		0.0031	48.4
	0.0034	67.7		0.0020	67.7		0.0037	67.7
	0.0044	96.6		0.0031	96.6		0.0053	96.6
	0.0072	145.0		0.0036	145.2		0.0075	145.0
6	0.0011	19.3	8	0.0145	18.9	9	0.0073	19.0
	0.0026	48.4		0.0393	47.2		0.0198	47.5
	0.0032	67.7		0.0399	66.6		0.0262	66.6
	0.0043	96.6		0.0505	95.3		0.0374	95.0
	0.0082	144.8		0.0751	143.0		0.0569	142.6
14	0.0013	19.2	15	0.0009	19.3	18	0.0015	19.2
	0.0030	48.2		0.0022	48.3		0.0026	48.3
	0.0049	67.4		0.0028	67.7		0.0037	67.6
	0.0066	96.2		0.0039	96.5		0.0051	96.4
	0.0100	144.4		0.0055	145.0		0.0065	144.9
20	0.0039	19.2	21	0.0004	19.4	22	0.0006	19.4
	0.0060	48.3		0.0009	48.5		0.0012	48.4
	0.0096	67.5		0.0014	67.8		0.0018	67.8
	0.0132	96.3		0.0017	96.8		0.0025	96.7
	0.0187	144.7		0.0024	145.3		0.0036	145.2
23	0.0015	19.3	26	0.0006	19.3			
	0.0026	48.4		0.0014	48.4			
	0.0032	67.8		0.0020	67.8			
	0.0053	96.6		0.0025	96.7			
	0.0073	145.1		0.0033	145.3			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

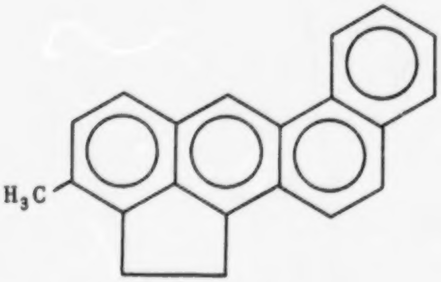
TABLE 4.20. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF DIBENZ[*a,h*]ANTHRACENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	20,461	1.690.971
4	2.07	34,929	1,687,404
5	2.28	18,361	805,292
6	0.72	18,882	2,622,453
8	0.15	1,759	1,172,847
9	0.11	2,506	2,277,875
14	0.48	14,497	3,020,262
15	0.95	25,302	2,663,317
18	0.66	20,192	3,059,425
20	1.30	7,345	565,014
21	1.88	55,697	2,962,603
22	1.67	39,809	2,383,765
23	2.38	19,254	808,991
26	1.48	39,840	2,691,870

4.7. 3-METHYLCHOLANTHRENE

3-Methylcholanthrene (20-methylcholanthrene) is an alkyl-substituted polynuclear aromatic hydrocarbon containing four aromatic rings and one five-membered ring. 3-Methylcholanthrene has the second lowest water solubility of the compounds studied. Its carbon number and molecular length are less than for dibenzanthracene; hence it is slightly less hydrophobic in nature. The physical properties of 3-methylcholanthrene are given in Table 4.21.

TABLE 4.21. PHYSICAL PROPERTIES OF 3-METHYLCHOLANTHRENE

Structure	
Molecular weight[a]	268.34
Melting point (°C)[a]	179-180
Boiling point (°C) at 80 mm[a]	280
Density[a]	1.28

[a] Merck Index. 9th ed.

The octanol-water partition coefficient (Kow) for 3-methylcholanthrene was determined over a range of aqueous concentrations with radiolabeled compound using the procedure given in Section 5.2. A Kow value of 2,632,000 was obtained. The water solubility of 3-methylcholanthrene was determined to be 0.00323 μg/ml by the procedure outlined in Section 5.3.

Batch equilibrium isotherms were determined using ^{14}C-labeled 3-methylcholanthrene obtained from New England Nuclear. Purity of the radiolabeled compound was verified by thin-layer chromatography. Appropriate amounts of 3-methylcholanthrene were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous phase concentrations (4.56 to 48.49 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 2 g:40 ml soil to solution ratio.

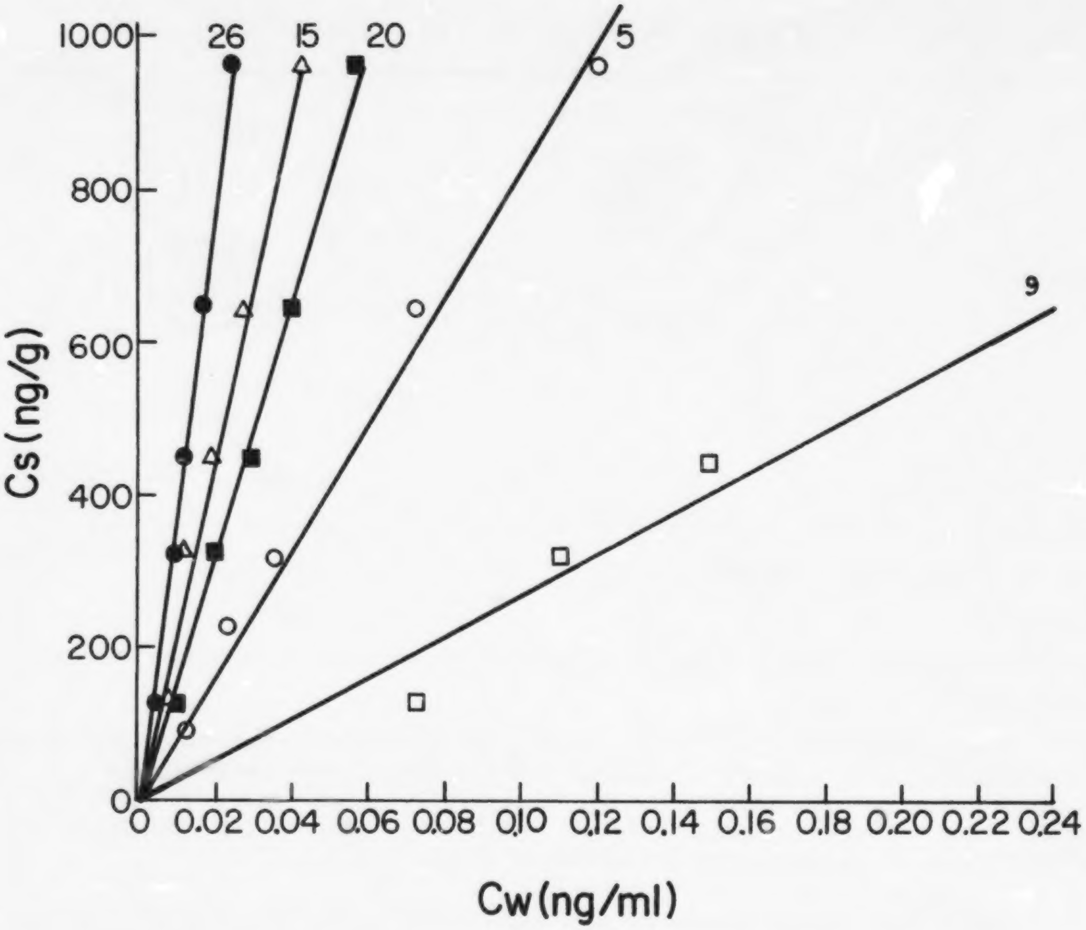


FIGURE 4.11. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 3-METHYLCHOLANTHRENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.22. 3-METHYLCHOLANTHRENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.0074	90	4	0.0043	91	5	0.0125	90
	0.0135	226		0.0082	227		0.0237	226
	0.0187	316		0.0107	317		0.0366	316
	0.0252	452		0.0153	454		0.0731	641
	0.0482	677		0.0219	680		0.1204	960
6	0.0094	128	8	0.048	125	9	0.053	125
	0.0198	320		0.128	313		0.111	314
	0.0288	448		0.292	622		0.149	440
	0.0400	640		0.407	936		0.242	625
14	0.0040	128	15	0.0062	128	18	0.0062	128
	0.0105	320		0.0118	321		0.0142	320
	0.0156	448		0.0189	449		0.0198	449
	0.0184	642		0.0274	641		0.0327	640
	0.0323	961		0.0427	961			
20	0.0092	128	21	0.0052	129	22	0.0068	128
	0.0202	320		0.0119	322		0.0167	321
	0.0302	448		0.0174	450		0.0208	449
	0.0401	641		0.0272	643		0.0321	641
	0.0570	961		0.0394	965		0.0444	963
23	0.0064	129	26	0.0041	129			
	0.0206	321		0.0107	322			
	0.0318	449		0.0121	451			
	0.0395	642		0.0178	644			
	0.0507	964		0.0243	966			

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[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

Isotherm suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours. The phases were separated by centrifugation.

Initial and final aqueous phase concentrations of 3-methylcholanthrene were determined by liquid scintillation counting. The amount of 3-methylcholanthrene sorbed by the soil/sediment phase was calculated from the difference between initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and degradation products by the procedure outlined in Section 5.4.1.

Representative isotherms are given in Figure 4.11. The isotherms were linear and gave good fits to the following equation:

$$Cs = Kp \cdot Cw \qquad (4\text{-}1)$$

The sorption data for 3-methylcholanthrene are given in Table 4.22; the values are averages of triplicate determinations. Linear partition coefficients and Koc values are given in Table 4.23. Regression of Kp against percent organic carbon gave a Koc value of 1,244,046 ($r^2 = 0.705$).

TABLE 4.23. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF 3-METHYLCHOLANTHRENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	15,140	1,251,210
4	2.07	30,085	1,453,404
5	2.28	8,273	362,845
6	0.72	15,820	2,197,250
8	0.15	2,257	1,504,538
9	0.11	2,694	2,449,190
14	0.48	30,627	6,380,703
15	0.95	23,080	2,429,456
18	0.66	20,642	3,127,521
20	1.30	16,231	1.248,534
21	1.88	24,506	1,303,532
22	1.67	20,972	1,255,821
23	2.38	17,127	719,633
26	1.48	37,364	2,524,581

The sorption of 3-methylcholanthrene and the other three polynuclear aromatic hydrocarbons studied (pyrene, dimethylbenzanthracene and dibenzanthracene) appears to be an example of hydrophobic sorption. For these and other compounds with very low water solubilities or high octanol-water partition coefficients, the main driving force in their sorption is related to the large increase in entropy of the system upon sorption of the organic out of the aqueous phase. The increase in entropy is due to the destruction of the highly structured water shell around the solvated organic molecule (14). The increasing sorption of these compounds with decreasing water solubility is primarily related to an ever decreasing solute-solvent interaction and possibly to an increasing sorbate-sorbent interaction due to increasing van der Waals bonding of the compounds to the soil or sediment humic materials.

The highly significant relationship between a compound's octanol-water partition coefficient and its degree of sorption by soils/sediments when normalized to an organic carbon basis (Koc) is due to the partitioning similarities in both systems. In soil systems and in sediment systems the aqueous phases are, respectively, the soil solution and the water column plus the interstitial water, and the organic phases are the humic materials.

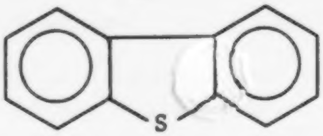
If compounds such as pyrene or 3-methylcholanthrene were placed in a land-fill containing organic materials that were soluble in or miscible with water (ethanol, acetone, etc.), the sorption characteristics of the compounds could be greatly altered with subsequent markedly increased mobilities. This decrease in sorption would be due to a strengthened solute-solvent interaction upon the addition of the soluble organic.

4.8. DIBENZOTHIOPHENE

Heterocyclic polynuclear aromatic compounds such as dibenzothiophene are added to the environment from a variety of sources and are subject to environmental concern due to their possible carcinogenic and/or mutagenic activities (37). Dibenzothiophene has been identified in used crankcase oil, on particulates in storm water runoff and on Delaware River sediments (38). In addition to oil spills and runoff from land-based oil use, heterocyclic sulfur compounds such as dibenzothiophene are added to the environment in coal gasification waste waters and in leachates from coal storage areas (2).

The physical properties of dibenzothiophene are given in Table 4.24.

TABLE 4.24. PHYSICAL PROPERTIES OF DIBENZOTHIOPHENE

Structure	
Molecular weight[a]	184.26
Melting point (°C)[a]	97-100
Boiling point (°C)[a]	332-333

[a] Aldrich catalog, 1979-80

The octanol-water partition coefficient for dibenzothiophene was determined over a range of aqueous concentrations using radiolabeled compound and the procedure given in Section 5.2. A Kow value of 24,000 was obtained. The water solubility of dibenzothiophene was determined to be 1.47 μg/ml by the procedure outlined in Section 5.3.

Batch equilibrium sorption isotherms were determined using ^{3}H-labeled dibenzothiophene that had been tritiated by the method described in Section 5.1.3. The unlabeled dibenzothiophene used in the tritiation procedure was obtained from Pfaltz and Bauer. Purity was verified using thin-layer chromatography. The sorption isotherms were determined in triplicate using a 4 g:40 ml solid to solution ratio with initial concentrations ranging from 154 to 1230 ng/ml. The isotherms were carried out in stainless steel centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 20 hours. Initial and final concentrations of dibenzothiophene in the solution phase were determined by liquid scintillation counting. The concentration of dibenzothiophene in the soil/sediment phase was determined by difference.

The results of both the sediment-water and the octanol-water partitioning experiments could be influenced by degradation of the compound to form different chemical products or by losses of the compound due to volatilization. Therefore, in each partitioning experiment with dibenzothiophene, a ^3H mass balance was determined to verify that there was no loss of compound from the system. High pressure liquid chromatography was used to determine if a significant quantity of the dibenzothiophene had been degraded. The ^3H mass balance was calculated from the total ^3H-labeled material in both the water and the sediment phases; prior to counting, the ^3H-labeled material in the sediment phase was converted to ^3H_2O using a Packard Model 306 sample oxidizer. The recovery of ^3H was 99+% in all partitioning experiments, and no evidence of dibenzothiophene degradation was observed by liquid chromatography.

The sorption of dibenzothiophene by sediment and soils produced basically linear isotherms which were described by the following equation:

$$Cs = Kp \cdot Cw \qquad (4\text{-}1)$$

where Cs is the amount sorbed in ng/g of soil or sediment, Cw is the equilibrium solution concentration in ng/ml, and Kp is the linear partition coefficient. Representative isotherms are shown in Figure 4.12. Average values for the sorption isotherm data for each soil and sediment are given in Table 4.25.

The Freundlich adsorption isotherm is represented by the following equation:

$$Cs = Kd \cdot Cw^{1/n} \qquad (4\text{-}3)$$

where Kd and 1/n are Freundlich constants. Equation 4-3 is equivalent to equation 4-1 when the exponential Freundlich constant (1/n) is equal to unity.

The linear partition or sorption constants and r^2 values for the fit of the data to equation 4-1 are given in Table 4.26. The Freundlich constants (Kd and 1/n) and their corresponding r^2 values are also given in Table 4.26. The 1/n values varied from 0.781 to 1.357 with a mean value of 0.996. The Kd values were expressed on a molar basis (19) and gave values similar to the linear partition coefficients (Kp) for the respective soils and sediments. Linear partition coefficients were used instead of Freundlich constants for subsequent correlation comparisons in order to keep the variation between samples expressed as one constant instead of two.

The organic carbon content of the sediments or soils was significantly correlated with Kp at the 1% level of probability, while other factors tested (e.g., total clay, clay mineralogy, CEC, surface area) were nonsignificant. When the Kp values were divided by their respective sediment or soil organic carbon contents, thus putting sorption on a uniform carbon basis, a unique constant (Koc) for nonpolar compounds was generated.

$$Koc = Kp/(\%OC/100) \qquad (2\text{-}1)$$

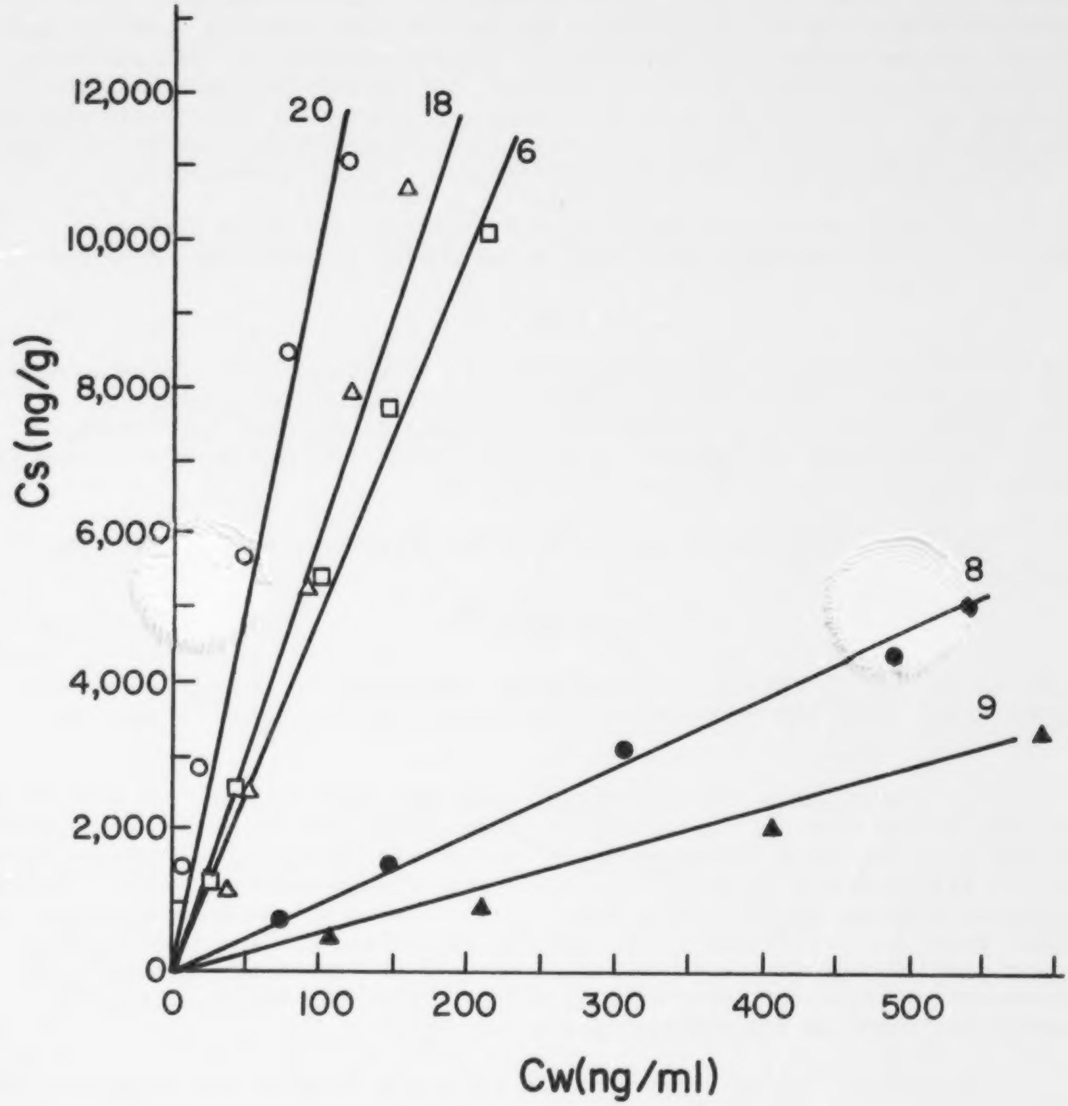


FIGURE 4.12. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF DIBENZOTHIOPHENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.25. DIBENZOTHIOPHENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	12.4	1413	4	9.6	1441	5	9.4	1444
	24.3	2832		17.9	2897		15.2	2923
	46.6	5683		31.1	5839		36.2	5788
	77.8	8447		46.3	8762		48.6	8739
	92.4	11376		64.8	11652		71.1	11589
6	39.2	1145	8	74.1	797	9	108.8	449
	54.3	2532		148.8	1588		211.8	957
	93.2	5218		305.4	3096		409.5	2055
	132.2	7903		486.1	4365		590.0	3325
	157.1	10729		634.3	5957		754.3	4757
14	25.8	1279	15	7.2	1466	18	18.9	1349
	48.0	2595		14.5	2930		39.2	2683
	96.9	5181		30.5	5846		74.5	5405
	147.3	7752		48.6	8739		120.3	8022
	213.4	10166		65.7	11643		167.6	10624
20	8.8	1450	21	4.0	1498	22	9.0	1448
	18.8	2887		10.1	2974		17.8	2897
	48.7	5663		20.3	5947		32.1	5830
	78.1	8444		32.5	8900		49.3	8732
	117.2	11128		42.5	11875		66.0	11640
23	3.0	1508	26	8.9	1449			
	7.6	3000		18.7	2888			
	15.7	5993		38.6	5764			
	23.9	8986		61.8	8607			
	30.1	11999		87.9	11421			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

TABLE 4.26. LINEAR PARTITION CONSTANTS (Kp) AND THEIR r^2 VALUES, AND MOLAR FREUNDLICH CONSTANTS (Kd and 1/n) AND THEIR r^2 VALUES FOR THE SORPTION OF DIBENZOTHIOPHENE BY SOILS AND SEDIMENTS.

Sample	Kp	r^2	Koc	Kd (molar)	1/n (molar)	r^2
B2	117.5	0.995	9711	118.0	1.007	0.992
4	180.6	0.989	8725	208.7	1.096	0.974
5	167.1	0.994	7329	167.1	0.993	0.979
6	60.8	0.970	8444	67.3	1.357	0.875
8	9.4	0.996	6267	4.1	0.916	0.991
9	5.8	0.985	5273	4.5	1.204	0.990
14	49.7	0.994	10354	49.5	0.966	0.966
15	179.9	0.996	18937	166.2	0.932	0.993
18	65.1	0.989	9864	65.4	0.957	0.998
20	101.4	0.983	7800	82.2	0.781	0.998
21	276.0	0.983	14681	224.9	0.880	0.996
22	176.3	0.997	10557	191.4	1.057	0.982
23	388.6	0.997	16328	304.8	0.892	0.994
26	134.5	0.989	9088	124.7	0.908	0.996

This constant is dependent on the properties of the compound being studied and independent of soil or sediment properties (11,15,19,39). Koc values calculated from the linear partition coefficients are given in Table 4.26. Regression of Kp against soil or sediment organic carbon content gave a Koc value of 11,230 ($r^2 = 0.904$).

Karickhoff *et al.* (15) demonstrated a significant relationship between the octanol-water partition coefficient (Kow) of a compound and its Koc value.

$$\log \text{Koc} = 1.00 \log \text{Kow} - 0.21 \qquad (4\text{-}5)$$

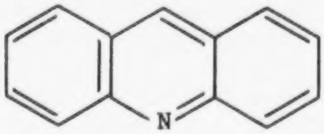
where Kow is a measure of compound partitioning between an aqueous phase and a liquid organic phase, octanol. The Kow value for dibenzothiophene was determined to be 24,000; this value gave a predicted Koc of 14,798 which was in good agreement with the Koc (11,230) obtained from the sorption experiments. Karickhoff *et al.* (15) found good agreement between measured Koc values and the Koc values predicted from Kow for a variety of compounds including benzene, naphthalene, anthracene and pyrene.

The sorption of dibenzothiophene and similar compounds appears to be an example of hydrophobic or nonpolar sorption (14). The sorption of dibenzothiophene occurs not because of a strong positive sorbate-sorbent interaction but rather because of a weak solute-solvent interaction. The weak solute-solvent interaction is a result of the nonpolar nature of dibenzothiophene and is manifested in its low water solubility (1.47 μg/ml). The less polar a compound is, the greater its solubility in octanol, the lower its solubility in water, and the greater its sorption; hence the relationship between increasing Kow values and increasing adsorption. This type of sorption has been referred to as hydrophobic sorption to emphasize the role of the weak solute-solvent interaction.

4.9. ACRIDINE

Nitrogen-heterocyclic compounds deserve special attention because they make up from 3 to 11 volume percent of the organic contaminants present in coal tar from the Synthane coal conversion process (2). Acridine (dibenzo-[*b,e*]pyridine; 2,3,5,6-dibenzopyridine), 2,2'-biquinoline and 13*H*-dibenzo-[*a,i*]carbazole were selected as representative compounds for the study of the sorption of N-heterocyclic compounds by soils and sediments. A brief discussion of factors affecting the sorption of N-heterocyclics is given in Section 4.11. The physical properties of acridine are given in Table 4.27.

TABLE 4.27. PHYSICAL PROPERTIES OF ACRIDINE

Structure	
Molecular weight (Aldrich catalog, 1979-80)	179.22
Melting point (°C) (Aldrich catalog, 1979-80)	107-110
Boiling point (°C) (Aldrich catalog, 1979-80)	346
Density (CRC Handbook, 1975-76)	1.005

The octanol-water partition coefficient (Kow) for acridine was determined over a range of aqueous concentrations using radiolabeled compound and the procedure described in Section 5.2. A Kow value of 4200 was obtained. The water solubility was determined to be 38.4 μg/ml by the procedure outlined in Section 5.3.

Batch equilibrium sorption isotherms were determined using ^{3}H-labeled acridine that had been tritiated by the method outlined in Section 5.1.3. The unlabeled acridine used in the tritiation procedure was obtained from Aldrich Chemical Co. (>99% pure). The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography.

An aqueous stock solution was prepared by evaporating (under a stream of N_2 gas) an appropriate quantity of purified ^{3}H-labeled acridine stock solution onto the lower walls of a glass container, adding ultrapure water and stirring for 24 hours. To remove any undissolved material, the aqueous stock solution was filtered through a 0.2μ Nuclepore filter. Ultrapure water was used to dilute the stock solution to the desired concentration levels for determining the isotherms. Batch equilibrium sorption isotherms were determined in triplicate on a 1:10 soil to solution ratio with initial acridine concentrations ranging from 0.29 to 1.74 μg/ml. Isotherm suspensions were shaken in stainless steel centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours. Kinetic studies showed that sorption equilibrium was attained after approximately nine hours.

Initial and final aqueous phase concentrations of acridine were determined by liquid scintillation counting. The concentration of acridine sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure outlined in Section 5.4.1.

Sorption of acridine by soils and sediments resulted in linear sorption isotherms over the entire concentration range studied. Average values for individual sorption isotherms are given in Table 4.28. Representative isotherms are shown in Figure 4.13.

Initially the data were fit to the Freundlich sorption isotherm equation:

$$Cs = Kd \cdot Cw^{1/n} \qquad (4\text{-}3)$$

Since 1/n values were very close to unity for all samples, the data were fit to a modified Freundlich equation where 1/n was forced to be 1.0. A summary of these data is given in Table 4.29. Regression of Kp against the soil or sediment organic carbon content produced a Koc value of 12,910 ($r^2 = 0.934$).

TABLE 4.28. ACRIDINE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (μg/ml)	Cs[c] (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)
B2	0.027	4.6	4	0.016	4.9	5	0.018	4.8
	0.065	11.9		0.036	12.5		0.042	12.3
	0.086	16.4		0.048	17.6		0.065	16.9
	0.126	23.4		0.076	24.8		0.086	24.5
	0.156	28.1		0.091	30.0		0.106	29.4
6	0.030	4.5	8	0.088	3.5	9	0.077	3.4
	0.070	11.5		0.222	8.6		0.208	8.0
	0.110	15.6		0.328	11.6		0.316	10.3
	0.167	21.8		0.470	16.5		0.451	14.8
	0.206	26.1		0.623	18.4		0.536	18.1
14	0.034	4.6	15	0.026	4.6	18	0.041	4.4
	0.069	12.1		0.061	11.8		0.077	12.0
	0.102	16.7		0.094	16.0		0.117	16.5
	0.164	23.3		0.136	22.8		0.220	21.8
	0.209	27.7		0.172	27.2		0.283	25.7
20	0.029	4.6	21	0.028	4.7	22	0.041	4.4
	0.062	12.0		0.064	11.9		0.110	10.8
	0.084	16.9		0.078	17.1		0.154	15.2
	0.129	23.8		0.116	24.3		0.221	21.7
	0.147	29.0		0.142	29.3		0.294	25.2
23	0.019	4.9	26	0.020	4.8			
	0.036	12.7		0.046	12.3			
	0.062	17.2		0.060	17.4			
	0.084	24.8		0.108	23.9			
	0.107	29.6		0.147	28.0			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

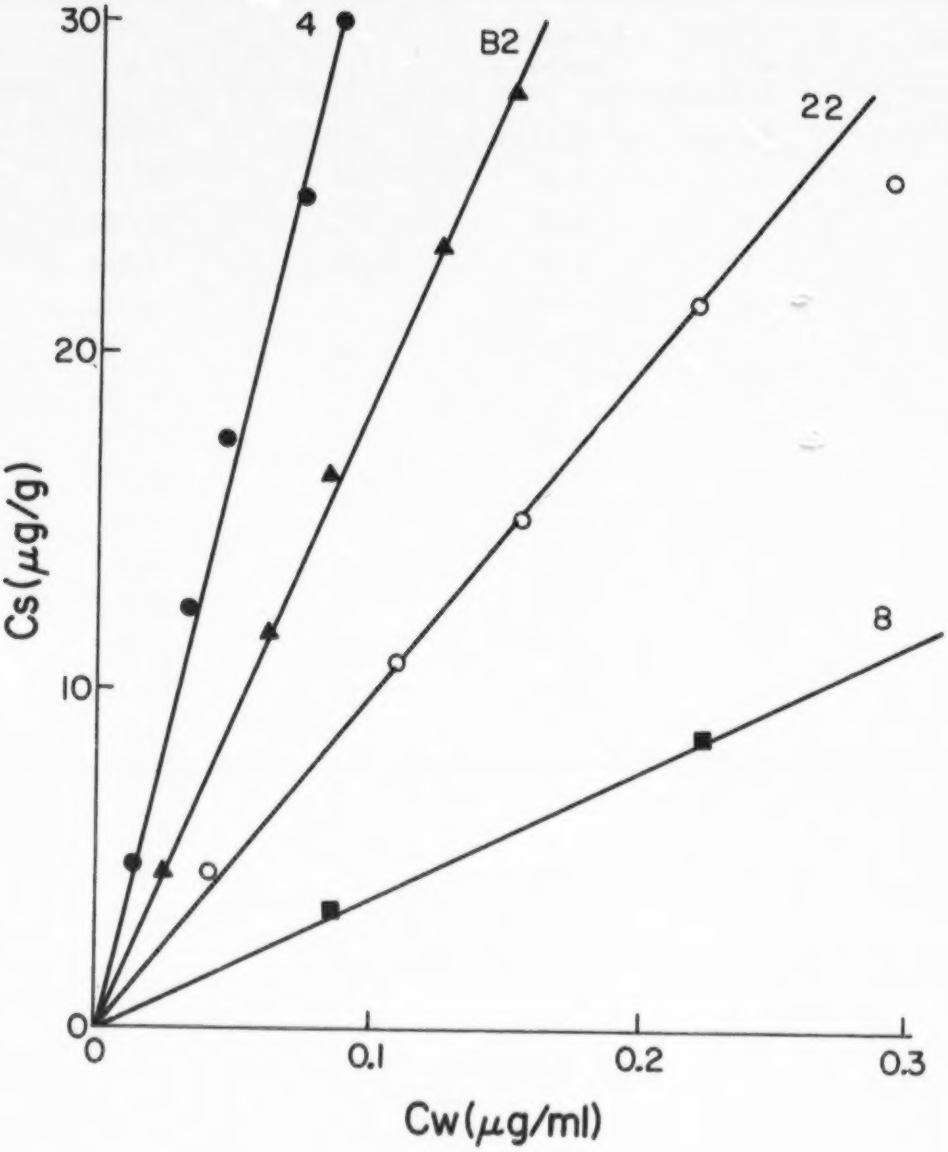


FIGURE 4.13. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF ACRIDINE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

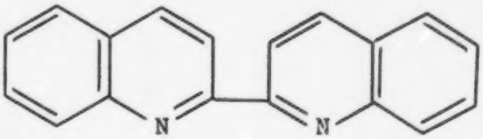
TABLE 4.29. MODIFIED FREUNDLICH PARTITION CONSTANTS (Kp, 1/n = 1) AND Koc VALUES FOR SORPTION OF ACRIDINE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	185	15,260
4	2.07	334	16,160
5	2.28	278	12,180
6	0.72	132	18,380
8	0.15	33	21,720
9	0.11	34	30,560
14	0.48	142	29,510
15	0.95	165	17,350
18	0.66	101	15,270
20	1.30	193	14,820
21	1.88	207	11,020
22	1.67	92	5,520
23	2.38	287	12,040
26	1.48	213	14,370

4.10. 2,2'-BIQUINOLINE

The physical properties of 2,2'-biquinoline (2,2'-biquinolyl) are given in Table 4.30.

TABLE 4.30. PHYSICAL PROPERTIES OF 2,2'-BIQUINOLINE

Structure	
Molecular weight (Aldrich catalog, 1979-80)	256.31
Melting point (°C) (Aldrich catalog, 1979-80)	193-196

The octanol-water partition coefficient (Kow) for biquinoline was determined over a range of aqueous concentrations using radiolabeled compound and the procedure outlined in Section 5.2. A Kow value of 20,200 was obtained. The water solubility was determined to be 1.02 μg/ml by the procedure described in Section 5.3.

Batch equilibrium sorption isotherms were determined using ^{3}H-labeled biquinoline that had been tritiated by the method outlined in Section 5.1.3. The unlabeled biquinoline used in the tritiation procedure was obtained from Aldrich Chemical Co. (99% pure). The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography. Appropriate amounts of biquinoline were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous phase concentrations (0.38 to 1.91 μg/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determinations. Sorption isotherms were determined in triplicate using a 4 g:40 ml soil to solution ratio. Isotherm suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for several hours. Kinetic studies showed that sorption equilibrium was attained within about one hour.

Initial and final aqueous phase concentrations of biquinoline were determined by liquid scintillation counting. The concentration of biquinoline

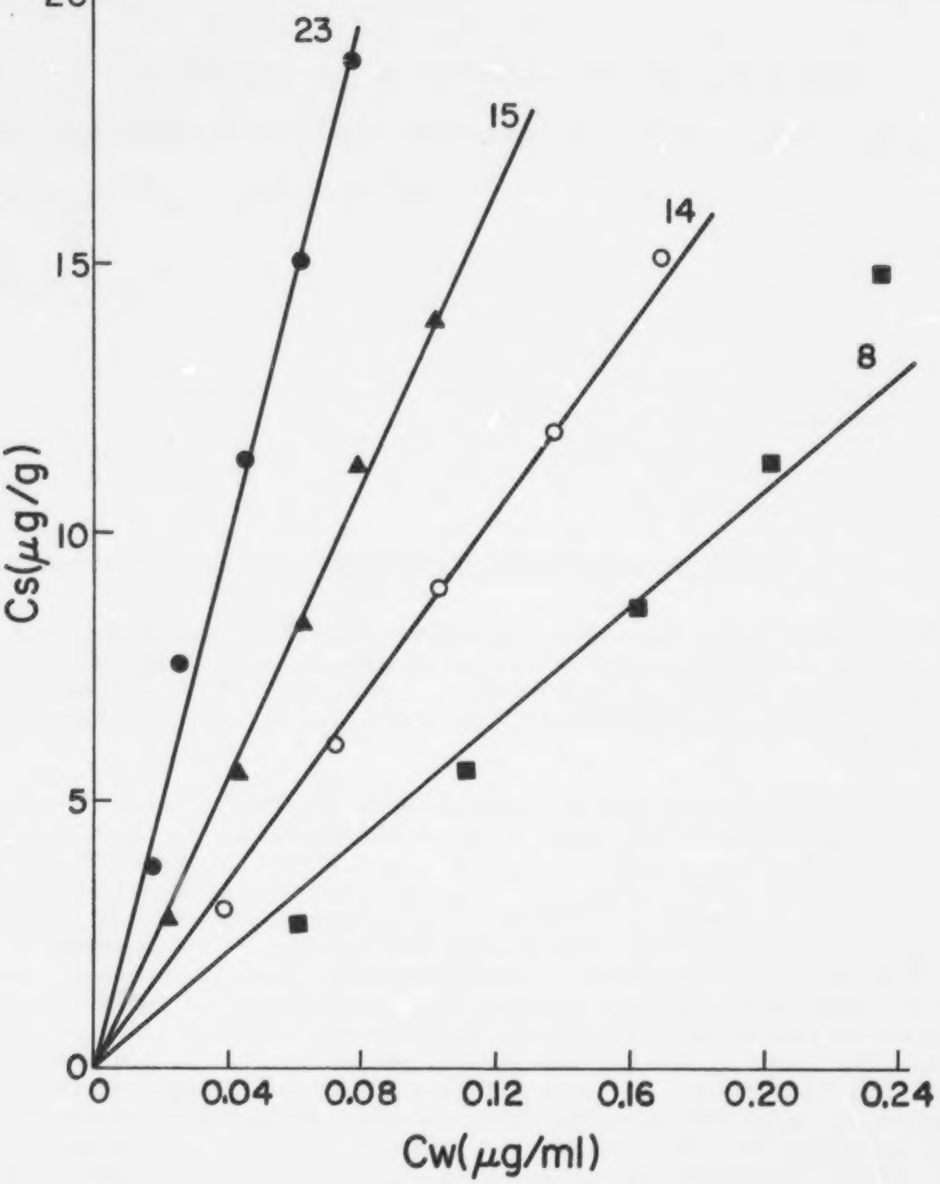


FIGURE 4.14. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 2,2'-BIQUINOLINE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.31. 2,2'-BIQUINOLINE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (μg/ml)	Cs[c] (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)	Sample	Cw (μg/ml)	Cs (μg/g)
B2	0.034	3.12	4	0.019	3.20	5	0.026	3.27
	0.068	6.25		0.038	6.41		0.045	6.68
	0.091	9.58		0.042	9.96		0.079	9.78
	0.110	13.02		0.064	13.10		0.085	13.46
	0.153	15.95		0.058	16.90		0.076	17.49
6	0.028	3.30	8	0.061	2.65	9	0.065	2.78
	0.042	6.93		0.112	5.53		0.115	5.88
	0.060	10.46		0.161	8.43		0.160	9.08
	0.079	13.96		0.204	11.48		0.197	12.42
	0.099	17.43		0.233	14.80		0.236	15.74
14	0.039	2.92	15	0.020	2.79	18	0.031	2.46
	0.070	6.01		0.043	5.53		0.045	5.26
	0.103	9.07		0.062	8.34		0.078	7.68
	0.138	12.09		0.078	11.23		0.096	10.38
	0.170	15.18		0.101	13.95		0.115	13.08
20	0.039	3.47	21	0.019	3.54	22	0.020	3.56
	0.080	6.89		0.037	7.11		0.042	7.09
	0.116	10.40		0.042	11.05		0.059	10.72
	0.139	14.16		0.068	14.42		0.085	14.14
	0.187	17.44		0.082	18.08		0.090	18.07
23	0.017	3.71	26	0.025	3.36			
	0.035	7.41		0.049	6.75			
	0.044	11.32		0.056	10.52			
	0.061	15.05		0.073	14.07			
	0.076	18.80		0.092	17.57			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure outlined in Section 5.4.1.

Sorption of biquinoline, like that of acridine, resulted in linear sorption isotherms. Representative isotherms are shown in Figure 4.14. Average values for individual sorption isotherms are given in Table 4.31. As in the case of acridine, the biquinoline sorption data were fit to a modified Freundlich equation. A summary of these data is given in Table 4.32. A regression of Kp against the organic carbon content of the soils and sediments produced a Koc value of 10,404 ($r^2 = 0.922$). As shown in Table 4.32, samples 8 and 9 had considerably higher calculated Koc values than the other samples studied. Both of these samples had organic carbon contents less than 0.2%. The possibility of error in the determination of such low organic carbon contents is large, and any such error is then magnified in those values (Koc) based on the low organic carbon content data.

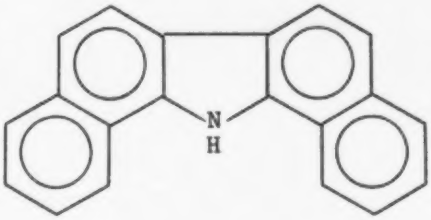
TABLE 4.32. MODIFIED FREUNDLICH PARTITION CONSTANTS (Kp, 1/n = 1) AND Koc VALUES FOR SORPTION OF 2,2'-BIQUINOLINE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	105	8,710
4	2.07	220	10,640
5	2.28	164	7,180
6	0.72	172	23,850
8	0.15	57	38,160
9	0.11	61	55,800
14	0.48	88	18,310
15	0.95	135	14,234
18	0.66	106	16,110
20	1.30	93	7,140
21	1.88	216	11,500
22	1.67	181	10,830
23	2.38	243	10,210
26	1.48	180	12,180

4.11. 13*H*-DIBENZO[*a*,*i*]CARBAZOLE

The third N-heterocyclic compound studied was 13*H*-dibenzo[*a*,*i*]carbazole (1,2,7,8-dibenzocarbazole). This compound is of interest because it is a known carcinogen (toxic substances list #HO54250). The physical properties of dibenzocarbazole are given in Table 4.33.

TABLE 4.33. PHYSICAL PROPERTIES OF 13*H*-DIBENZO[*a*,*i*]CARBAZOLE

Structure	
Molecular weight (Aldrich catalog, 1979-80)	267.33
Melting point (°C) (Aldrich catalog, 1979-80)	220-221

The octanol-water partition coefficient (Kow) for dibenzocarbazole was determined over a range of aqueous concentrations using radiolabeled compound and the procedure described in Section 5.2. A Kow value of 2,514,000 was obtained. The water solubility was determined to be 0.0104 μg/ml by the procedure outlined in Section 5.3.

Batch equilibrium sorption isotherms were determined using ^3H-labeled dibenzocarbazole that had been tritiated by the method given in Section 5.1.3. The unlabeled dibenzocarbazole used in the tritiation procedure was obtained from Aldrich Chemical Co. (>99% pure). The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography. Appropriate amounts of dibenzocarbazole were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous phase concentrations (9.02 to 36.08 μg/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 2 g:40 ml soil to solution ratio. Isotherm suspensions were shaken in the centrifuge tubes with

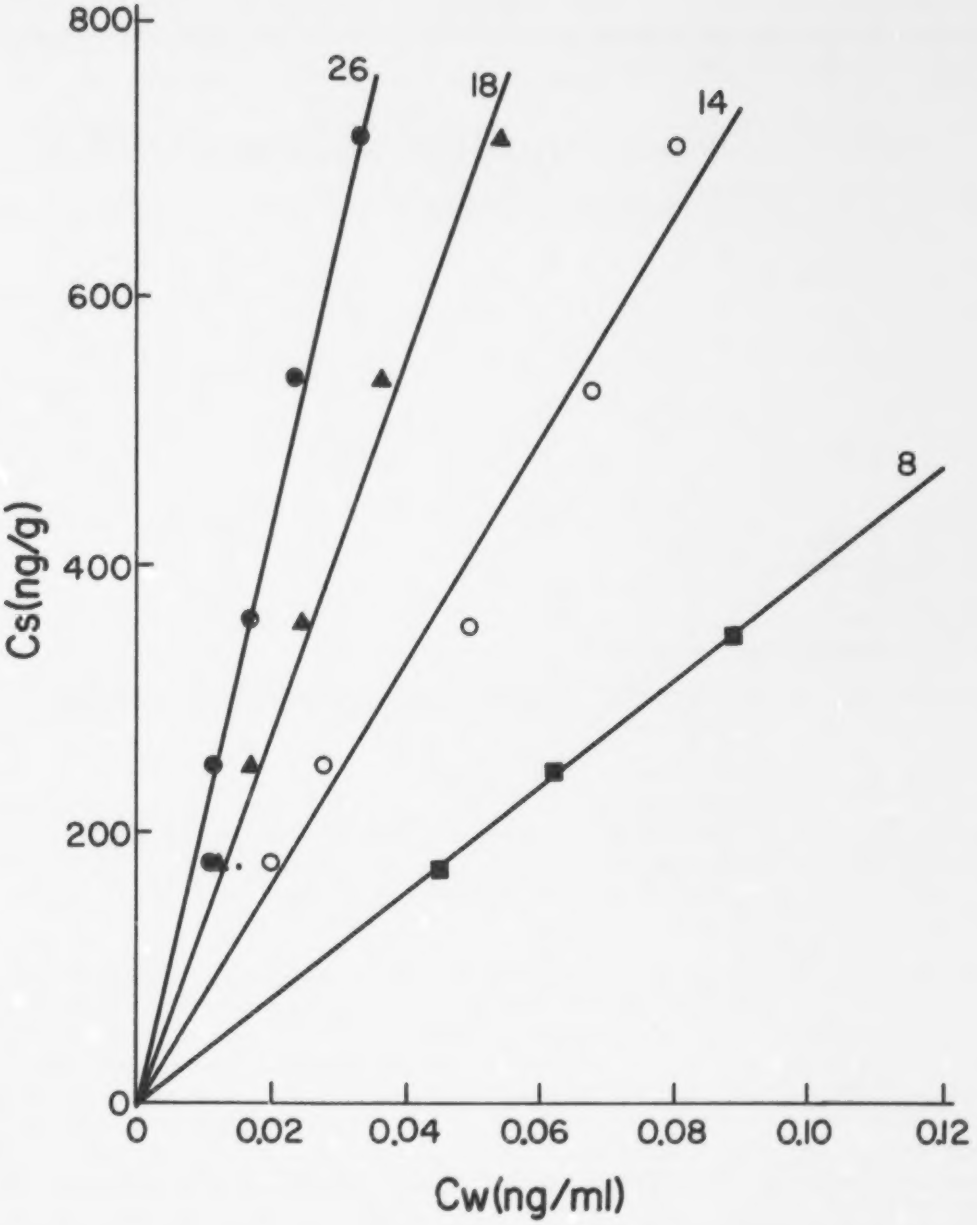


FIGURE 4.15. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 13*H*-DIBENZO-[*a,i*]CARBAZOLE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.34. 13*H*-DIBENZO[*a*,*i*]CARBAZOLE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.0071	179	4	0.0082	179	5	0.0158	179
	0.0116	251		0.0108	251		0.0206	250
	0.0132	358		0.0166	359		0.0264	358
	0.0176	538		0.0198	539		0.0372	537
	0.0212	717		0.0261	718		0.0455	717
6	0.0182	179	8	0.0447	174	9	0.153	175
	0.0219	250		0.0613	243		0.186	246
	0.0312	358		0.0888	347		0.343	348
	0.0407	537		0.1768	514		0.532	521
	0.0545	716		0.2299	686		0.741	694
14	0.0192	177	15	0.0134	179	18	0.0114	179
	0.0278	248		0.0158	251		0.0168	251
	0.0497	352		0.0267	358		0.0242	358
	0.0679	529		0.0402	537		0.0361	537
	0.0801	708		0.0538	717		0.0537	715
20	0.0138	178	21	0.0108	179	22	0.0102	179
	0.0189	249		0.0179	251		0.0131	251
	0.0241	356		0.0188	359		0.0233	357
	0.0350	534		0.0364	537		0.0267	537
	0.0435	713		0.0367	718		0.0392	716
23	0.0135	179	26	0.0103	179			
	0.0213	249		0.0110	251			
	0.0236	357		0.0171	359			
	0.0322	537		0.0233	538			
	0.0539	714		0.0338	717			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours. The phases were separated by centrifugation.

The initial and final aqueous phase concentrations of dibenzocarbazole were determined by liquid scintillation counting. The concentration of dibenzocarbazole sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure outlined in Section 5.4.1.

Sorption of dibenzocarbazole, like that of the other two N-heterocyclic compounds, resulted in linear sorption isotherms. Representative isotherms are shown in Figure 4.15. Average values for individual isotherms are given in Table 4.34. Modified Freundlich partition constants (Kp, where 1/n = 1) were calculated from individual isotherm values and presented in Table 4.35. A regression of Kp against soil or sediment organic carbon content produced a Koc value of 1,055,926 ($r^2 = 0.830$).

TABLE 4.35. MODIFIED FREUNDLICH PARTITION CONSTANTS (Kp, 1/n = 1) AND Koc VALUES FOR SORPTION OF 13*H*-DIBENZO[*a,i*]CARBAZOLE BY SOILS AND SEDIMENTS

Sample	% Organic Carbon	Kp	Koc
B2	1.21	29,610	2,447,100
4	2.07	25,800	1,246,170
5	2.28	14,640	642,150
6	0.72	12,570	1,745,520
8	0.15	3,080	2,056,030
9	0.11	980	890,610
14	0.48	8,134	1,694,550
15	0.95	13,480	1,419,110
18	0.66	14,100	2,136,570
20	1.30	15,490	1,191,150
21	1.88	17,040	906,520
22	1.67	18,000	1,078,030
23	2.38	13,900	583,930
26	1.48	21,620	1,460,730

The data in Table 4.35 show a 30-fold variation between the lowest and the highest Kp values; the extremes in Koc values differed by about four-fold. The dominant soil/sediment physical property accounting for sorption was the organic carbon content, a finding that was consistent for all three N-heterocyclic compounds studied. Coefficients for correlation of dibenzocarbazole Kp with selected soil/sediment properties are given in Table 4.36.

TABLE 4.36. CORRELATION (r^2) OF 13*H*-DIBENZO[*a*,*i*]CARBAZOLE Kp WITH SELECTED SOIL/SEDIMENT PROPERTIES FOR THE 14 SOILS AND SEDIMENTS STUDIED

Property	r^2
% Total clay	0.14
% Expanding clay	0.18
% Organic carbon	0.66[a]
pH	0.18
CEC	0.20

[a] Significant at the 1% level of probability.

The sorption data for the representative N-heterocyclics chosen for this study gave good fits to the Freundlich sorption isotherm equation

$$Cs = Kd \cdot Cw^{1/n} \tag{4-3}$$

Individual Kd values varied considerably with both the soil or sediment and the specific compound. In all cases the 1/n values were quite close to unity, indicating linear sorption isotherm behavior; the data also gave good fits to the modified Freundlich equation where 1/n is forced to equal unity. Representative sorption isotherms illustrate graphically the linearity; data are given for plotting all isotherms, if desired.

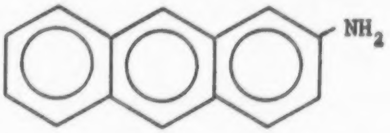
The dominant soil physical property affecting sorption of N-heterocyclics is the organic carbon content of the soil or sediment. A simple correlation of Kp with percent organic carbon content for all three compounds is significant at the 0.01% level of probability. None of the other physical properties measured (pH, CEC, % sand, % silt, % clay) were significantly correlated with Kp.

The relationships between Koc and Kow and between Koc and water solubility (discussed in Section 2) appeared to be valid for all three N-heterocyclic compounds studied. The results of this study would imply that the factors controlling sorption of N-heterocyclics are not significantly different from those controlling sorption of polynuclear aromatic hydrocarbons.

4.12. 2-AMINOANTHRACENE

Anthracene-9-carboxylic acid, 2-aminoanthracene and 6-aminochrysene were chosen as examples of substituted polynuclear aromatic hydrocarbons. The amine and carboxylic acid functional groups of these compounds greatly modify the hydrophobic nature of the parent compounds. These compounds were chosen near the completion of the contract to provide a test of the limitations of the hydrophobic sorption concept. The factors affecting the sorption of these compounds are discussed in Section 4.14 following the presentation of the sorption data for each of the substituted polynuclear aromatic hydrocarbons. The physical properties of 2-aminoanthracene (2-anthramine) are given in Table 4.37.

TABLE 4.37. PHYSICAL PROPERTIES OF 2-AMINOANTHRACENE

Structure	
Molecular weight (Aldrich catalog, 1979-80)	193.25
Melting point (°C) (Aldrich catalog, 1979-80)	238-241

The octanol-water partition coefficient (Kow) of 2-aminoanthracene was determined over a range of aqueous concentration using radiolabeled compound and the procedure given in Section 5.2. A value of 13,400 was obtained. The water solubility of 2-aminoanthracene was determined to be 1.30 μg/ml by the procedure outlined in Section 5.3.

Batch equilibrium isotherms were determined using ^{3}H-labeled 2-aminoanthracene that had been tritiated by the procedure given in Section 5.1.3. The unlabeled 2-aminoanthracene used in the tritiation procedure was obtained from Aldrich Chemical Co. The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography. Appropriate amounts of 2-aminoanthracene were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous phase concentrations (0.64 to 13.65 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 4 g:40 ml soil to solution ratio.

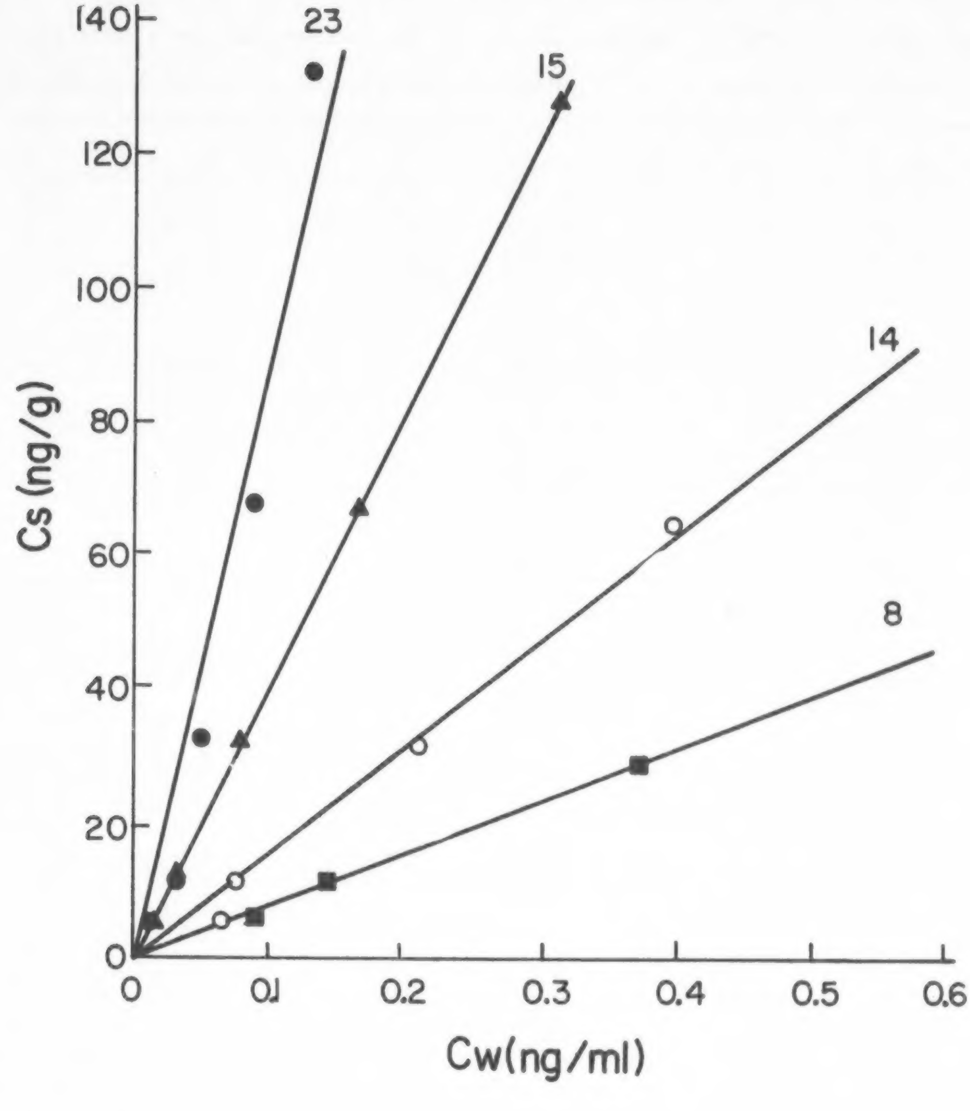


FIGURE 4.16. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 2-AMINO-ANTHRACENE BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.38. 2-AMINOANTHRACENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.031	5.8	4	0.025	5.9	5	0.024	5.9
	0.048	12.2		0.016	12.9		0.037	12.4
	0.107	32.7		0.121	32.5		0.128	32.0
	0.185	67.2		0.194	67.2		0.234	65.9
	0.383	128.6		0.373	129.0		0.394	127.7
6	0.152	3.6	8	0.089	5.0	9	0.093	5.0
	0.107	11.2		0.143	11.0		0.269	9.0
	0.199	31.2		0.375	29.1		0.343	29.6
	0.236	66.6		0.908	57.0		0.713	60.1
	0.409	128.8		1.253	117.1		0.963	121.6
14	0.064	5.4	15	0.016	6.0	18	0.024	5.9
	0.072	12.1		0.030	12.4		0.047	12.1
	0.210	31.7		0.076	33.0		0.092	32.9
	0.398	64.9		0.169	66.7		0.120	68.4
	0.867	123.1		0.313	128.4		0.470	126.0
20	0.020	5.8	21	0.023	5.8	22	0.031	5.8
	0.069	11.0		0.058	11.7		0.016	12.9
	0.102	31.7		0.077	33.0		0.071	33.4
	0.146	66.5		0.123	68.0		0.158	67.9
	0.247	128.8		0.230	130.7		0.241	131.6
23	0.012	6.0	26	0.015	6.0			
	0.031	12.2		0.024	12.5			
	0.051	33.3		0.069	33.0			
	0.088	68.3		0.101	68.3			
	0.131	132.4		0.177	131.6			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

Isotherm suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 24 hours.

Initial and final aqueous phase concentrations of 2-aminoanthracene were determined by liquid scintillation counting. The concentration of 2-aminoanthracene sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure described in Section 5.4.1.

Representative isotherms are given in Figure 4.16. The isotherms were linear and gave good fits to the following equation:

$$Cs = Kp \cdot Cw \tag{4-1}$$

The sorption data for 2-aminoanthracene are given in Table 4.38; the values are averages of three determinations. Linear partition coefficients and Koc values are given in Table 4.39. Regression of Kp against percent organic carbon in the soils or sediments gave a Koc value of 28,129 ($r^2 = 0.871$).

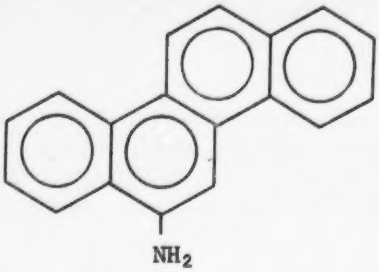
TABLE 4.39. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF 2-AMINOANTHRACENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	321.6	26,580
4	2.07	329.2	15,904
5	2.28	304.1	13,336
6	0.72	259.5	36,039
8	0.15	79.0	52,659
9	0.11	103.7	94,276
14	0.48	145.1	30,225
15	0.95	391.9	41,248
18	0.66	283.0	42,878
20	1.30	458.7	35,287
21	1.88	531.9	28,292
22	1.67	502.1	30,069
23	2.38	875.2	36,772
26	1.48	688.7	46,537

4.13. 6-AMINOCHRYSENE

6-Aminochrysene (6-chrysenamine) was chosen of one representative of substituted polynuclear aromatic hydrocarbons containing functional groups that could greatly modify their hydrophobic nature. The physical properties of 6-aminochrysene are given in Table 4.40.

TABLE 4.40. PHYSICAL PROPERTIES OF 6-AMINOCHRYSENE

Structure	
Molecular weight (Aldrich catalog, 1979-80)	243.31
Melting point (°C) (Aldrich catalog, 1979-80)	209-211.5

The octanol-water partition coefficient (Kow) of 6-aminochrysene was determined over a range of aqueous concentrations using radiolabeled compound and the procedure outlined in Section 5.2. A value of 96,600 was obtained. The water solubility of 6-aminochrysene was determined to be 0.155 μg/ml by the procedure described in Section 5.3.

Batch equilibrium isotherms were run using ^{3}H-labeled 6-aminochrysene that had been tritiated by the procedure given in Section 5.1.3. The unlabeled aminochrysene used in the tritiation procedure was obtained from Aldrich Chemical Co. The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography. Appropriate amounts of aminochrysene were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous phase concentrations (1.81 to 36.3 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 4 g:40 ml solid to solution ratio. Isotherm suspensions were shaken in the centrifuge tubes with teflon-covered lids in a

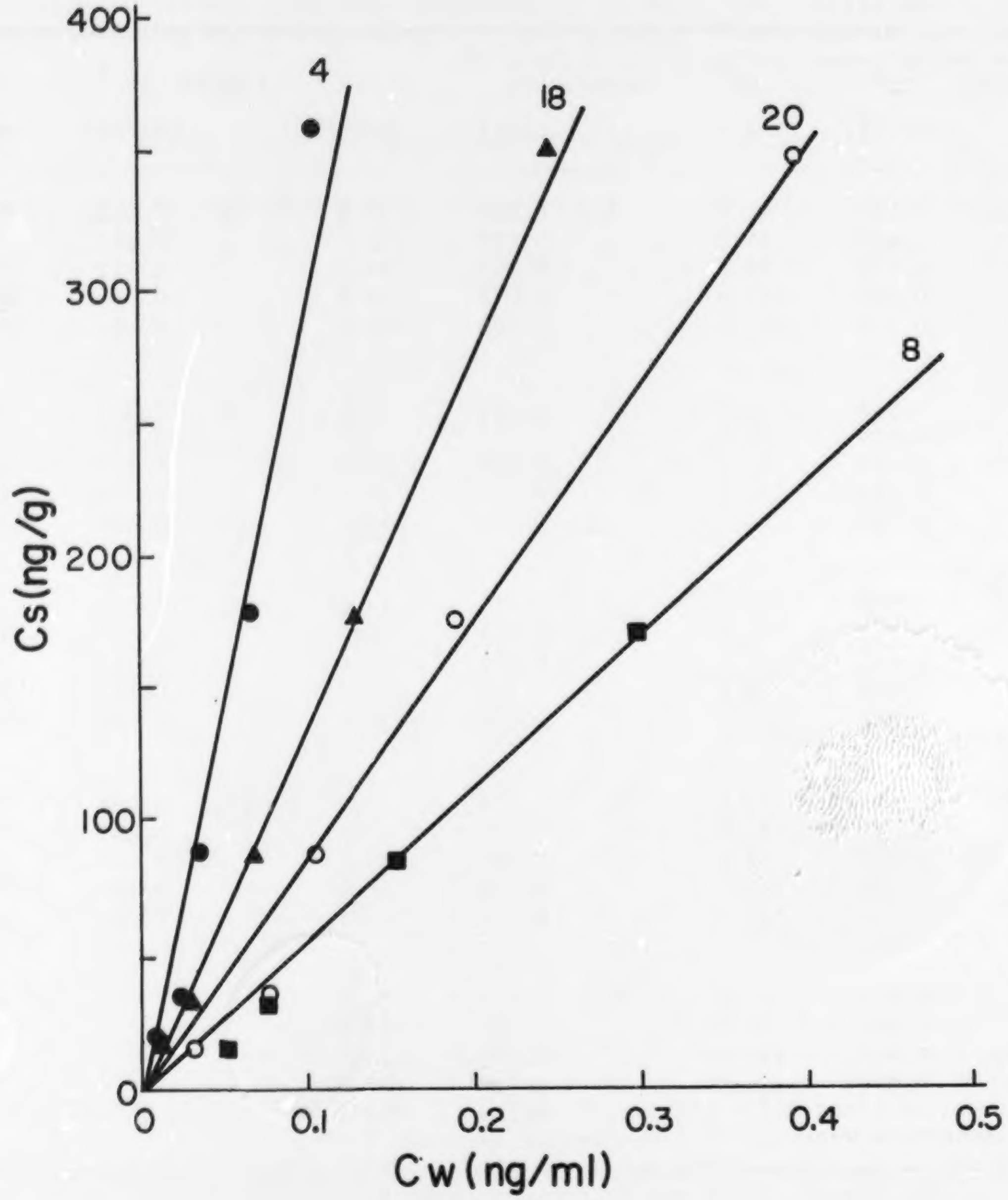


FIGURE 4.17. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF 6-AMINOCHRYSENE BY SOILS AND SEDIMENTS
Numbers refer to soil or sediment samples.

TABLE 4.41. 6-AMINOCHRYSENE SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (ng/ml)	Cs[c] (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)	Sample	Cw (ng/ml)	Cs (ng/g)
B2	0.015	17.6	4	0.008	17.8	5	0.017	17.5
	0.029	35.3		0.025	35.5		0.012	35.9
	0.055	89.2		0.032	89.9		0.032	89.9
	0.062	177.6		0.064	178.9		0.038	179.7
	0.193	356.6		0.104	359.5		0.084	360.2
6	0.040	16.6	8	0.051	16.4	9	0.049	16.5
	0.039	35.0		0.073	33.9		0.080	33.6
	0.083	88.2		0.150	86.0		0.137	86.4
	0.144	176.2		0.296	171.1		0.274	171.9
	0.323	352.2		0.579	343.7		0.466	347.4
14	0.059	16.1	15	0.020	17.4	18	0.019	17.5
	0.075	33.8		0.055	34.5		0.030	35.3
	0.152	85.9		0.072	88.6		0.063	88.9
	0.193	174.6		0.124	176.9		0.125	176.8
	0.312	352.6		0.268	354.1		0.244	354.9
20	0.033	17.0	21	0.026	17.2	22	0.026	17.2
	0.076	33.8		0.030	35.3		0.082	33.6
	0.103	87.6		0.041	89.6		0.104	87.5
	0.187	174.8		0.069	178.7		0.111	177.3
	0.394	349.9		0.120	359.0		0.191	356.6
23	0.011	17.7	26	0.035	16.9			
	0.031	35.3		0.057	34.4			
	0.046	179.4		0.066	88.8			
	0.079	360.4		0.120	177.0			
				0.169	357.4			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

temperature-controlled shaking water bath at 25°C for 20 hours. After equilibration the phases were separated by centrifugation.

Initial and final aqueous phase concentrations of 6-aminochrysene were determined by liquid scintillation counting. The concentration of 6-aminochrysene sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and degradation products by the procedure outlined in Section 5.4.1.

Representative isotherms are given in Figure 4.17. The isotherms were linear and gave good fits to the linear partition equation (4-1). The sorption data for 6-aminochrysene are given in Table 4.41; the values are averages of three determinations. Linear partition coefficients and Koc values are given in Table 4.42. Regression of Kp against soil or sediment organic carbon content gave a Koc value of 143,355 ($r^2 = 0.944$).

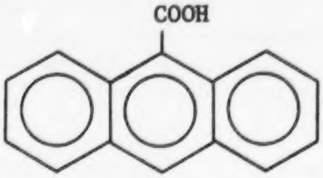
TABLE 4.42. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF 6-AMINOCHRYSENE BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	1,736	143,427
4	2.07	3,116	150,519
5	2.28	3,972	174,232
6	0.72	1,079	149,817
8	0.15	573	382,185
9	0.11	686	624,022
14	0.48	924	192,553
15	0.95	1,292	136,025
18	0.66	1,424	215,835
20	1.30	872	67,070
21	1.88	2,616	139,149
22	1.67	1,459	87,363
23	2.38	3,923	164,844
26	1.48	1,689	114,108

4.14. ANTHRACENE-9-CARBOXYLIC ACID

Anthracene-9-carboxylic acid was the third compound chosen to represent the substituted polynuclear aromatic hydrocarbons. Anthracene-9-carboxylic acid forms an anion upon dissociation of the carboxyl group while 2-aminoanthracene and 6-aminochrysene form cations upon protonation of the amine groups. The physical properties of anthracene-9-carboxylic acid are given in Table 4.43.

TABLE 4.43. PHYSICAL PROPERTIES OF ANTHRACENE-9-CARBOXYLIC ACID

Structure	
Molecular weight (Aldrich catalog, 1979-80)	222.24
Melting point (°C) (Aldrich catalog, 1979-80)	214 (decomposes)

The octanol-water partition coefficient (Kow) of anthracene-9-carboxylic acid was determined over a range of aqueous concentrations using radiolabeled compound and the procedure outlined in Section 5.2. A value of 1300 was obtained. The water solubility of anthracene-9-carboxylic acid was determined to be 85.0 μg/ml by the procedure described in Section 5.3.

Batch equilibrium isotherms were run using ^{3}H-labeled anthracene-9-carboxylic acid that had been tritiated by the procedure outlined in Section 5.1.3. The unlabeled anthracene-9-carboxylic acid used in the tritiation procedure was obtained from Aldrich Chemical Co. The tritiated compound was purified by microdistillation followed by preparative thin-layer chromatography. Appropriate amounts of anthracene-9-carboxylic acid were plated from acetone solution (under a stream of N_2 gas) onto the walls of stainless steel centrifuge tubes. These amounts represented the initial aqueous concentrations (3.85 to 79.94 ng/ml) that would have been present if the compound had been added as aqueous solution. Exact values for initial aqueous concentrations were determined by pipetting the same amounts of stock solution into scintillation vials for counting as were pipetted into the tubes for the isotherm determination. Sorption isotherms were determined in triplicate using a 4 g:40 ml solid to solution ratio. Isotherm suspensions were shaken in the centrifuge tubes with teflon-covered lids in a temperature-controlled shaking water bath at 25°C for 20 hours. The phases were separated by centrifugation.

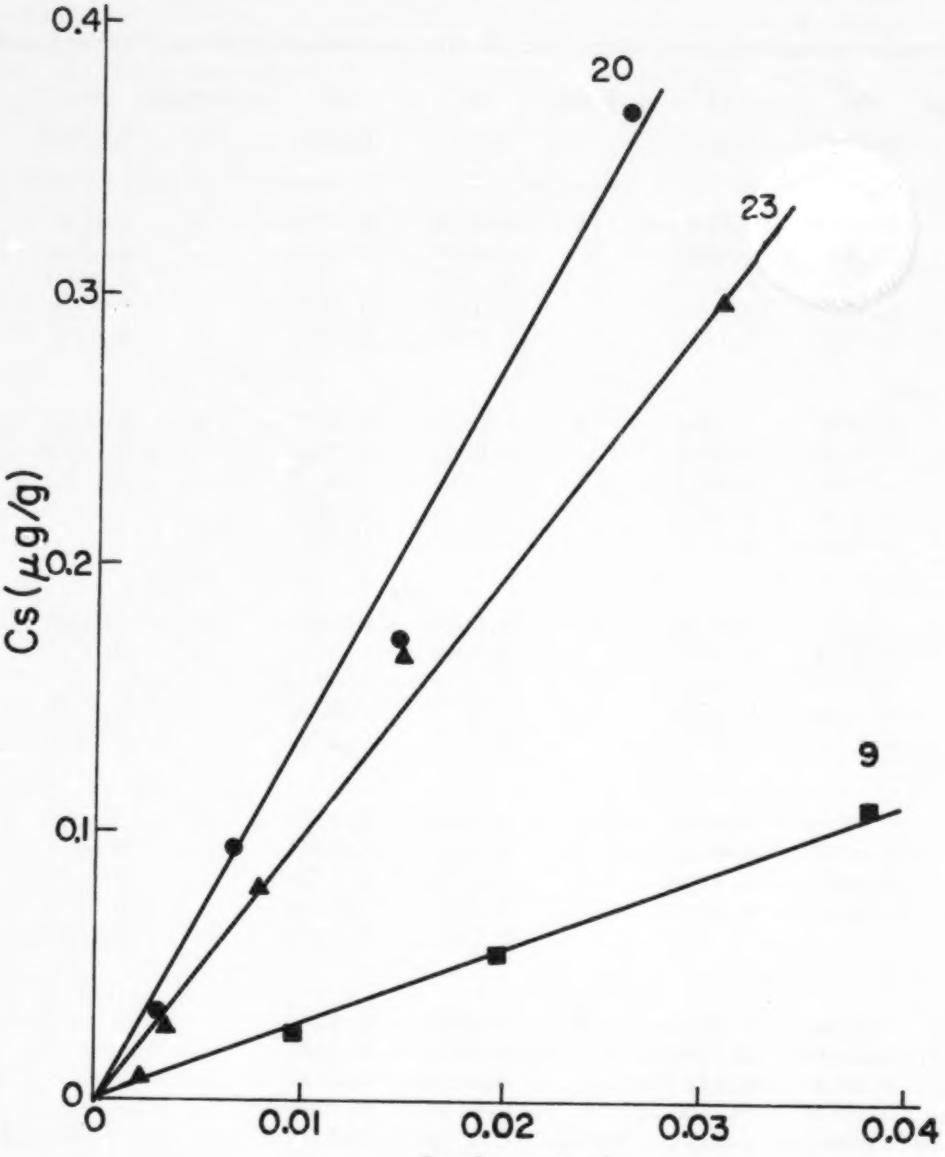


FIGURE 4.18. REPRESENTATIVE ISOTHERMS FOR THE SORPTION OF ANTHRACENE-9-CARBOXYLIC ACID BY SOILS AND SEDIMENTS

Numbers refer to soil or sediment samples.

TABLE 4.44. ANTHRACENE-9-CARBOXYLIC ACID SORPTION ISOTHERM DATA[a]

Sample	Cw[b] (µg/ml)	Cw[c] (µg/g)	Sample	Cw (µg/ml)	Cw (µg/g)	Sample	Cw (µg/ml)	Cs (µg/g)
B2	0.0014	0.0144	4	0.0016	0.0128	5	0.0014	0.0120
	0.0030	0.0289		0.0035	0.0233		0.0032	0.0207
	0.0096	0.0409		0.0095	0.0516		0.0090	0.0379
	0.0163	0.1362		0.0153	0.1684		0.0159	0.1233
	0.0366	0.1750		0.0385	0.1804		0.0299	0.2525
6	0.0006	0.0282	8	0.0009	0.0204	9	0.0098	0.0247
	0.0030	0.0261		0.0037	0.0093		0.0198	0.0555
	0.0089	0.0429		0.0094	0.0221		0.0378	0.1115
	0.0154	0.1359		0.0195	0.0385			
	0.0347	0.1717		0.0380	0.0680			
14	0.0017	0.0116	15	0.0020	0.0064	18	0.0020	0.0051
	0.0032	0.0292		0.0040	0.0146		0.0037	0.0162
	0.0087	0.0625		0.0116	0.0129		0.0094	0.0436
	0.0146	0.1776		0.0235	0.0286		0.0186	0.0987
	0.0304	0.3070		0.0409	0.1280		0.0436	0.0591
20	0.0028	0.0328	21	0.0008	0.0245	22	0.0012	0.0185
	0.0066	0.0934		0.0032	0.0244		0.0028	0.0333
	0.0144	0.1721		0.0086	0.0559		0.0090	0.0576
	0.0257	0.3693		0.0159	0.1402		0.0185	0.1142
				0.0342	0.2117		0.0368	0.2004
23	0.0018	0.0092	26	0.0003	0.0354			
	0.0030	0.0305		0.0017	0.0581			
	0.0076	0.0787		0.0065	0.1203			
	0.0148	0.1700		0.0139	0.2352			
	0.0303	0.2990		0.0419	0.2601			

[a] Values are averages of triplicate determinations.

[b] Cw is the equilibrium aqueous concentration.

[c] Cs is the amount sorbed by the soil or sediment sample.

Initial and final aqueous concentrations of anthracene-9-carboxylic acid were determined by liquid scintillation counting. The concentration of anthracene-9-carboxylic acid sorbed by the soil/sediment phase was determined from the difference between the initial and final radioactivity levels in the aqueous phase. Final solution concentrations were corrected for radiolabeled impurities and/or degradation products by the procedure described in Section 5.4.1.

Representative isotherms are given in Figure 4.18. The isotherms were linear and gave good fits to the linear partition equation (4-1). Sorption data for anthracene-9-carboxylic acid are given in Table 4.44; the values are averages of three determinations. Linear partition coefficients and Koc values are given in Table 4.45. Regression of Kp against soil or sediment organic carbon content gave a Koc value of 422 ($r^2 = 0.751$).

TABLE 4.45. LINEAR PARTITION COEFFICIENTS (Kp) AND Koc VALUES FOR THE SORPTION OF ANTHRACENE-9-CARBOXYLIC ACID BY SOILS AND SEDIMENTS

Sample	% Organic carbon	Kp	Koc
B2	1.21	5.27	436
4	2.07	5.49	265
5	2.28	7.96	349
6	0.72	5.47	760
8	0.15	1.84	1,227
9	0.11	2.82	2,564
14	0.48	10.03	2,090
15	0.95	2.66	280
18	0.66	1.78	270
20	1.30	13.27	1,021
21	1.88	6.45	343
22	1.67	5.59	335
23	2.38	9.88	415
26	1.48	7.50	507

The addition of hydrophilic functional groups to a hydrophobic compound will greatly increase the water solubility of the compound. Anthracene has a water solubility of 0.073 µg/ml (15) while 2-aminoanthracene and anthracene-9-

carboxylic acid have respective water solubilities of 1.30 and 85.0 µg/ml. The addition of a hydrophobic group such as a methyl group will decrease water solubility (15).

The hydrophilic functional group can affect sorption in different ways. If the functional group is involved in a specific reaction (e.g., cation exchange) with the soil or sediment, then the concept of the solute-solvent interaction dictating the degree of sorption will no longer be valid, and sorption will be much greater than predicted from the water solubility or Kow value. The sorption of benzidine is such an example. If the functional group does not enter into a specific reaction with the soil or sediment, then its effect will only be manifested in the solute-solvent interaction. In this case sorption will still be highly correlated with the compound's water solubility and/or Kow value. Anthracene-9-carboxylic acid, 2-aminoanthracene and 6 aminochrysene are examples of the latter case.

SECTION 5

EXPERIMENTAL METHODS

5.1. PREPARATION AND TRITIATION OF COMPOUNDS

All of the compounds used in the present study were available commercially in relatively pure form. Those exhibiting a level of purity below 95% were successfully purified by the procedure outlined below. Because many of the compounds are light-sensitive, the various manipulative and analytical procedures were carried out in the presence of either darkness or subdued light. Furthermore, because many of the compounds are subject to atmospheric oxidation, all containers (e.g., tubes, flasks, developing tanks) were flooded with N_2 to maintain an anaerobic atmosphere.

5.1.1. Chromatographic Analyses

5.1.1.1. Thin-Layer Chromatography

The most frequently used procedure for identifying suspected compounds and determining their degree of purity in the present investigation was thin-layer chromatography (TLC). The procedure is rapid, relatively simple, reproducible, and generally reliable.

The TLC developing tanks containing appropriate solvent systems (see Table 5.1) were flooded with N_2 and allowed to equilibrate at room temperature for about one hour. Commercially available 20x20-cm and 5x20-cm glass plates coated with 0.25 or 0.5-mm-thick layers of silica gel G (non-fluorescent) were activated in a 100°C oven for one hour and stored in a desiccator box until used. A vertical line was scribed with a dissecting needle about one-eighth inch in from the side edges of each plate so that solvent migration on the bulk of the plate would not be affected by the change in capillarity at the edge of the plate where the coating ceased. A horizontal solvent front line 15 cm above the origin (which was marked lightly with a pencil 1.5 cm from the bottom) and vertical lines demarking lanes were similarly scribed. A 5x20-cm plate accommodated up to three lanes easily, and a 20x20-cm plate a dozen or more lanes.

In most cases, approximately 5 μg of compound in an appropriate solvent (e.g., ether) were spotted at the origin in a given lane. After development of the chromatogram in the appropriate solvent system (see Table 5.1), the plate was air-dried or gently blown dry in a stream of N_2. Examination of the plate under short-wave ultraviolet (UV) light revealed fluorescent spots against a dark (UV-absorbing) background. (N.B. All compounds used in the present study fluoresced under UV light.) While the

TABLE 5.1. TYPICAL Rf VALUES FOR 14 ENERGY-RELATED COMPOUNDS IN SELECTED THIN-LAYER CHROMATOGRAPHIC SOLVENT SYSTEMS

Compound	Solvent System[a]	Approximate Rf Value
Pyrene	*n*-Hexane : diethyl ether (95:5)	0.73
7,12-Dimethylbenz [*a*]anthracene	*n*-Hexane : diethyl ether (100:3)	0.64
Dibenz [*a*, *h*]anthracene	*n*-Hexane : diethyl ether (100:3)	0.70
3-Methylcholanthrene	*n*-Hexane : diethyl ether (100:3)	0.61
Dibenzothiophene	*n*-Hexane : diethyl ether (100:3)	0.75
Acridine	Benzene : methanol (95:5)	0.73
2,2'-Biquinoline	Methylene chloride : methanol (98:2)	0.73
13*H*-Dibenzo [*a*, *i*]carbazole	*n*-Hexane : diethyl ether (50:50)	0.70
Acetophenone	Benzene : acetone (95:5)	0.69
1-Naphthol	Benzene : methanol (9:1)	0.57
Benzidine	Benzene : methanol (7:3)	0.70
2-Aminoanthracene	Benzene : methanol : HAc (9:1:0.05)	0.67
6-Aminochrysene	Benzene : methanol (95:5)	0.71
Anthracene-9-carboxylic acid	Benzene : methanol : HAc (7:3:0.05)	0.56

[a] All solvents were measured on a volume basis; HAc = glacial acetic acid.

plate was still under the UV light, outlines of spots were marked with a pencil. The Rf value of a compound was calculated as the distance (in cm) from the origin to the center of the spot divided by the distance from the origin to the solvent front. In the indicated solvent systems, the Rf values listed in Table 5.1 were expected.

5.1.1.2. Gas-Liquid Chromatography

The second most frequently used procedure for identifying suspected compounds, measuring the degree of purity of the compounds, and quantitating compounds in the present investigation was gas-liquid chromatography (GLC). Like TLC, this procedure is rapid, relatively uncomplicated, reproducible and generally reliable.

A Varian Aerograph Series 1860 Gas Chromatograph with flame ionization detector was utilized for determinations involving a 12-foot OV-17 column. The hydrogen flow rate for this instrument was maintained at 32 ml/min, the air flow rate at 270 ml/min, and the nitrogen (carrier gas) flow rate at 25 ml/min. The injection port temperature was 225°C, and the detector temperature 300°C. Column temperatures were either maintained isothermally or programmed at a rate of 8° per minute, depending upon the compound.

A Varian Aerograph Series 2700 Gas Chromatograph with flame ionization detector was used when a Carbowax column or a 6-foot OV-17 column was preferred. Both chromatographs were operated in conjunction with a Hewlett-Packard Model 3380A Recording Integrator. The hydrogen flow rate for the Series 2700 instrument was maintained at 25 ml/min, the air flow rate at 230 ml/min, and the nitrogen flow rate at 25 ml/min. The injection port temperature was 175°C, and the detector temperature 310°C. The temperatures of both columns were maintained isothermally.

Silanized six and 12-foot glass columns were packed with 3% OV-17 on 80/100-mesh Supelcoport (Supelco, Inc., Bellefonte, PA). These two columns were used for the detection and quantitation of most of the compounds in the present study. Under the indicated conditions, the retention times presented in Table 5.2 were expected.

A silanized 6-foot stainless steel column was packed with 0.2% Carbowax 1500 on 60/80-mesh Carbopack C (Supelco). This column was used primarily for the detection and quantitation of acetophenone and small quantities of α-naphthol in water samples. Under the indicated conditions, the retention times of α-naphthol and acetophenone were ∿24 and ∿30 minutes, respectively. Because the retention times were rather long, triplicate injections could be made at 5-minute intervals, thus minimizing the time necessary for replicated results.

5.1.2. Purity and Purification Procedures

5.1.2.1. Determination of Specific Activity and Radiochemical Purity

All radiolabeled compound preparations purchased from commercial sources or tritiated in the laboratory were analyzed to determine the exact

TABLE 5.2. TYPICAL GAS-LIQUID CHROMATOGRAPHIC CONDITIONS AND RETENTION TIMES FOR 14 ENERGY-RELATED COMPOUNDS

Compound	Column[a]	Column Temperature Operation	Column Temperature (°C)	Approx. Retention Time (min)
Pyrene	OV-17 (12')	Isothermal	185	6.5
7,12-Dimethylbenz[*a*]anthracene	OV-17 (12')	Programmed[b]	150-280	16
Dibenz[*a,h*]anthracene	OV-17 (6')	Isothermal	275	2.7
3-Methylcholanthrene	OV-17 (12')	Isothermal	300	10
Dibenzothiophene	OV-17 (12')	Isothermal	170	4.2
Acridine	OV-17 (6')	Isothermal	130	3.1
2,2'-Biquinoline	OV-17 (6')	Isothermal	210	5.4
13*H*-Dibenzo[*a,i*]carbazole	OV-17 (12')	Isothermal	300	4.0
Acetophenone	Carbowax (6')	Isothermal	190	30
1-Naphthol	OV-17 (12') Carbowax (6')	Isothermal Isothermal	140 190	3.7 24
Benzidine	OV-17 (6')	Isothermal	185	3.6
2-Aminoanthracene	OV-17 (6')	Isothermal	185	3.1
6-Aminochrysene	OV-17 (6')	Isothermal	260	2.5
Anthracene-9-carboxylic acid	OV-17 (6')	Isothermal	140	3.0

[a] OV-17 = 3% OV-17 on 80/100-mesh Supelcoport; Carbowax = 0.2% Carbowax 1500 on 60/80-mesh Carbopack C.

[b] All program rates were 8° per minute.

amount of radioactivity (in disintegrations per minute, dpm) and the total weight of compound contained therein. In addition, each compound was analyzed for radiochemical purity by means of TLC (Table 5.3).

The radiolabeled compound was dissolved or diluted in an appropriate solvent (e.g., acetone) in a 15-ml screw-capped centrifuge tube at the rate of 50 μCi/5 ml. In order to minimize evaporation and maximize compound stability, this stock solution was stored under N_2 at 0°C between uses.

Triplicate one-μl samples of the stock solution were subjected to liquid scintillation counting in order to determine the exact number of dpm present in the solution. In the case of radiolabeled compounds purchased from commercial sources, the total mg of compound received was calculated from the specific activity provided by the source and the dpm determined above. In the case of compounds tritiated in the laboratory, the total mg were determined by GLC using pure unlabeled compound as the standard. The weight was verified gravimetrically by evaporating a known quantity of solution to dryness in a tared tube under a stream of N_2 and reweighing the tube and contents in order to obtain the net weight. From the dpm and the weight values, the specific activity of the tritiated compound was calculated.

A TLC tank containing the appropriate solvent system (see Table 5.1) was flooded with N_2 and allowed to equilibrate at room temperature for about one hour. The stock solution was spotted at the rate of ∿10,000 dpm/spot along with a small amount of unlabeled standard solution on a 5x20-cm 0.25-mm - thick silica gel G plate. The plate was developed to the solvent front and then air-dried or gently blown dry in a stream of N_2. The location of the unlabeled standard was visualized under UV light and recorded. One-cm segments from the solvent front to the bottom of the plate were scraped into vials of Aquasol (New England Nuclear, Boston, MA) for liquid scintillation counting.

The quantity of radioactivity in the segments corresponding to the unlabeled standard was calculated as a percentage of the total radioactivity in the sample lane. If the compound was >95% pure, no further purification was necessary. If the purity was <95%, the compound was subjected to the purification procedure outlined below.

5.1.2.2. Purification of Compounds

The following modifications of the analytical thin-layer chromatography procedure for determining radiochemical purity (described above) were sufficient to convert it into a preparative procedure for purification of the compounds used in this study. The compound in question was banded (without the presence of unlabeled standard) at the rate of about 15 μCi per 20x20-cm plate for radiolabeled compounds or 100 mg per 20x20-cm plate for unlabeled compounds on a 0.5-mm-thick silica gel G plate. After development of the chromatogram, the fluorescent band with the appropriate Rf value (see Table 5.1) was stipple-outlined by means of a dissecting needle. (This band was always the major band on the plate.) The band was immediately scraped into a 50-ml screw-capped centrifuge tube, and the compound eluted from the silica gel with three 20-ml volumes of appropriate solvent (e.g., acetone) under N_2.

TABLE 5.3. RADIOCHEMICAL PURITY INFORMATION FOR 14 ENERGY-RELATED COMPOUNDS USED IN THIS STUDY

Compound	Label Position	Source[a]	Purity Specified by Source (%)	Purity Det'd in This Lab (%)	Purity after Purif'n (%)	Specific Activity (mCi/mmol)
Pyrene	$^3H(G)$	UI	-	99.6	FPU[b]	300
7,12-Dimethylbenz-[*a*]anthracene	7,12-di-methyl-^{14}C	NEN	98	80.6	99.2	114.65
Dibenz[*a*,*h*]anthracene	$^3H(G)$	NEN	96	89.3	97.7	35.14[c]
3-Methylcholanthrene	6-^{14}C	NEN	97	94.2	97.1	60.2
Dibenzothiophene	$^3H(G)$	UI	-	88.6	98.2	9.76
Acridine	$^3H(G)$	UI	-	81.3	97.1	0.111, 0.136[d]
2,2'-Biquinoline	$^3H(G)$	UI	-	80.5	97.0	0.0868
13*H*-Dibenzo-[*a*,*i*]carbazole	$^3H(G)$	UI	-	88.7	99.5	185
Acetophenone	7-^{14}C	ICN	>98	90.7	98.1	5.8
1-Naphthol	1-^{14}C	ICN	>98	97.1	FPU	10.0
Benzidine	$^{14}C(U)$	NEN	98	98.3	FPU	25.7
2-Aminoanthracene	$^3H(G)$	UI	-	87.0	97.1	24.9
6-Aminochrysene	$^3H(G)$	UI	-	91.2	99.4	55.2
Anthracene-9-carboxylic acid	$^3H(G)$	UI	-	84.2	97.4	0.926

[a] NEN = New England Nuclear; ICN = ICN Chemical and Radioisotope Div.; UI = tritiation carried out during present investigation.

[b] FPU = further purification unnecessary.

[c] Ci/mmol.

[d] Two batches of acridine were tritiated.

The eluates were combined and concentrated to a small volume under a stream of N_2. Any residual silica gel present in the concentrated eluate was removed by centrifugation. The eluate was then subjected to analytical TLC to check for purity. All compounds purified in this manner showed only a single spot on TLC and a single peak on GLC; all radiolabeled compounds were >95% pure.

5.1.3. Tritiation

Five of the compounds selected for investigation were available commerciallly in ^{14}C-labeled form and one in ^{3}H-labeled form. The remaining compounds were not available in radiochemical form except by custom synthesis which is expensive. Tritiation of the latter compounds by a modification of the procedures of Hilton and O'Brien (40) and Lu *et al.* (41) proved to be an effective and relatively inexpensive means of radiolabeling these compounds.

Five millimoles (0.56 g) of P_2O_5 were placed in a 5-ml round-bottom flask that was fitted with a desiccating U-tube and chilled in a slurry of acetone-dry ice in a small crystallizing dish. By means of a disposable syringe and needle, 12 millimoles (0.21 ml) of $^{3}H_2O$ were allowed to run down the side of the flask where the water froze. The flask was removed from the slurry bath so that the water gradually melted and reacted with the P_2O_5 to form tritiated phosphoric acid. When the reaction was complete, the reaction mixture was bubbled with BF_3 gas for about 10 minutes. A magnetic stirring bar was added to the flask, followed by an appropriate quantity of tritiatable compound (50-500 mg) dissolved in a small quantity of a suitable organic solvent (about one ml). Characteristics of a suitable organic solvent include immiscibility with water, a minimum number of exchangeable hydrogens, and the capacity to dissolve the tritiatable compound at a level of 50-500 mg/ml. The reaction mixture was stirred overnight at room temperature with the drying tube in place; the hydrogen-tritium exchange occurred during this period.

The reaction mixture was transferred to a 200-ml round-bottom flask; 50 ml of water and 50 ml of solvent, part of which had been used to rinse the reaction vessel, were added along with a magnetic stirring bar. The flask was loosely stoppered (small piece of aluminum foil inserted between stopper and flask) and the mixture stirred overnight at room temperature. The flask contents were transferred to a 500-ml separatory funnel; the aqueous phase was removed and saved. The solvent phase was extracted with two 100-ml volumes of water-solvent (2:1, v/v); the solvent phases were transferred to a 500-ml round-bottom flask. The combined aqueous phases were extracted with about 150 ml of solvent, the aqueous phase discarded, and the solvent phase added to the round-bottom flask. Sufficient methanol was added to provide a total volume of about 350 ml.

The flask was placed in a heating mantle over a magnetic stirrer, a stirring bar added, and a microdistillation apparatus connected. Consecutive 25-ml fractions were collected and monitored for radioactivity. In cases where the initial solvent was cyclohexane, the distillate was biphasic; both phases were monitored for radioactivity. Distillation was continued until the radioactivity in the distillate reached a low plateau, at which point the initial solvent had been distilled off completely. During distillation, for every 50 ml of distillate collected, 50 ml of methanol were added to the distillation flask. After the low radioactivity plateau was reached, the microdistillation apparatus was disconnected, a few grams of anhydrous Na_2SO_4 were added to the distillation flask, and the contents were allowed to stand for a few hours at room temperature to dry off residual water.

The liquid phase was transferred to a fresh 500-ml flask, followed by several rinses of the previous flask, and evaporated to near-dryness on a rotary evaporator. The flask contents were transferred, with rinses, to a 15-ml screw-capped centrifuge tube. The solution was concentrated to a reasonable volume (e.g., 10 ml) under a stream of N_2. Radiochemical purity of each tritiated compound was determined by the TLC procedure outlined earlier in this section. If not ∿99% pure, the compound was purified by the preparative TLC procedure described earlier in this section. Aliquots of a solution of the pure compound were subjected both to liquid scintillation counting in order to determine radioactive content and to GLC along with standard solutions to determine concentration. A known volume of the solution was evaporated to dryness in a tared tube under a stream of N_2 and the weight of the compound per given volume of solution verified. The specific activity of the tritiated compound was calculated.

For all compounds tritiated during the present study, tritiation involved the exchangeable hydrogens on the aromatic rings. The rather stringent conditions inherent in the tritiation procedure were sufficient to remove any label from the substituent groups of 6-aminochrysene, 2-aminoanthracene and anthracene-9-carboxylic acid. Nevertheless, in order to verify that no residual tritium remained on the substituent groups, the following procedure was utilized.

Two small aliquots (e.g., 0.2 ml) of a methanolic solution of each tritiated amino-substituted compound were diluted to 5 ml with water (pH 6). One solution was adjusted to pH 10-11 with 1N NaOH in order to ionize the substituent group, mixed well, allowed to stand for a few minutes, and then readjusted to pH 6 with 1N HCl. Dilution of the carboxylic acid-substituted compound in water (at pH 6) was sufficient to ionize the substituent group, and therefore only a single solution of this compound was prepared.

The solutions were extracted three times with equal volumes of methylene chloride. The volume of the extracted aqueous phases remained at 5 ml; the volumes of the extracts were recorded. Both the aqueous phases and the extracts were sampled in triplicate (1.0 ml for the former, 0.2 ml for the latter) for liquid scintillation counting. The percent radioactivity remaining in the aqueous phase after extraction was the same for both solutions (pH-adjusted and unadjusted) and amounted to less than 0.2% of the total radioactivity present in the extract and the extracted aqueous phase. If the substituent groups of the three compounds had been tritiated, the pH-adjusted aqueous phases would have contained 5-10% of the total radioactivity after extraction.

5.1.4. Radioactivity Measurements

The radioactive content of samples, fluid or dry, was measured by liquid scintillation counting in a Packard Model 2425 Tri-Carb Liquid Scintillation Spectrometer. Fluid samples included stock solutions, extracts, partition phases, eluates, filtrates and distillates. Scrapings from chromatogram plates were the only dry samples counted directly. Aquasol was used as the counting cocktail for all direct samples, and Permafluor V (Packard Instrument Co., Inc., Downers Grove, IL) or Monophase-40 (Packard) for samples processed in a Packard Model 306 Sample Oxidizer. The latter samples were primarily soil and sediment phases from sorption isotherm determinations. ^{14}C from oxidized samples was collected as $^{14}CO_2$ in Carbo-Sorb (Packard) and added to Permafluor V for counting; ^3H from oxidized samples was collected as ^3H_2O directly in Monophase-40. All samples were counted for 10-minute periods. All counts were corrected for background radioactivity and counting efficiency.

5.2. OCTANOL-WATER PARTITIONING PROCEDURE

The partitioning of a solute between two immiscible solvent phases has become a handy reference characteristic. In addition, when the partitioning of the solute into one phase (especially a volatile phase) is very much greater than into the other phase, the technique becomes a useful means of solute extraction. The literature contains numerous articles describing partitioning methodology and interpretations. Portions of the methods of Leo *et al.* (42), Chiou *et al.* (43), Karickhoff *et al.* (15) and Karickhoff (44) were utilized in the present investigation to develop a procedure (Figure 5.1) that gives reproducible results with organic compounds possessing limited water solubility.

For compounds with known or predicted low water solubility, such as the polynuclear aromatic hydrocarbons (PAH), the pure radiolabeled compound was used without the addition of unlabeled compound in order to provide significant levels of radioactivity in the aqueous phases. For compounds with moderate-to-high water solubility, such as acetophenone or α-naphthol, a sufficient quantity of pure unlabeled compound was added to the radiolabeled compound to avoid excessively high levels of radioactivity in the octanol phases.

Using a predicted Kow of the compound to calculate the quantity of compound necessary to provide a statistically significant level of radioactivity in the aqueous phase, a sufficient quantity of radiolabeled compound was dissolved or diluted in a suitable solvent (e.g., acetone). An appropriate amount of solution was shell-evaporated under a stream of N_2 onto the lower walls of each of triplicate foil-covered screw-capped Erlenmeyer flasks; 50-ml flasks were used for volumes ranging from 10 to 15 ml, and 500-ml flasks for volumes ranging from 100 to 300 ml. Five ml of 1-octanol that had been purified by the method of Karickhoff *et al.* (15) were added to each flask. The flasks were shaken at moderate speed on a Burrell Wrist-Action shaker at room temperature (24°C) for one to two hours to ensure full dissolution of the compound in the octanol. Octanol-saturated ultrapure (>10 megohm/cm) water was added to each flask at the rate of 5-10 ml for moderately water-soluble compounds and 100-300 ml for the less water-soluble compounds. The flasks were flooded with N_2 and shaken at moderate speed for 15 minutes.

Pure radiolabeled compound

↓

Dissolve in suitable solvent

↓

Shell-evaporate (under N_2) on lower walls of
triplicate foil-covered screw-capped 500-ml Erlenmeyer flasks

↓

Add 5 ml purified 1-octanol to each flask

↓

Shake (wrist-action shaker), moderate speed, 1-2 hours, room temperature

↓

Add 300 ml octanol-saturated ultrapure (>10 megohm/cm) water to each flask;
flood flasks with N_2

↓

Shake at moderate speed, 15 minutes, room temperature

↓

Transfer upper portion of mixture to glass (Corex) centrifuge tubes;
centrifuge at 30,000xg, 20 minutes, 24°C;
discard lower (uncentrifuged) portion of mixture

↓

Repeat centrifugation if interface is not clear

↓

Sample octanol phase (10 µl in triplicate) for liquid scintillation counting;
remove and return octanol phase to original Erlenmeyer flask

↓

Remove and discard all residual octanol at interface
(including some aqueous phase, if necessary)

↓

Carefully sample aqueous phase (1.0 ml in triplicate)
for liquid scintillation counting
(make sure that pipette is wiped free of any residual octanol)

↓

Calculate Kow
(Kow = dpm/ml octanol phase ÷ dpm/ml aqueous phase)

↓

Repeat partitioning procedure with fresh octanol-saturated ultrapure water
until Kow value remains constant (indicative of compound purity)

↓

By means of HPLC, determine % of radioactivity in aqueous phase
actually representing parent compound; correct Kow value accordingly

FIGURE 5.1. PROTOCOL FOR DETERMINING THE OCTANOL-WATER PARTITION COEFFICIENT OF A HYDROPHOBIC ORGANIC COMPOUND

The full contents of the small flasks were transferred to 15-ml Corex centrifuge tubes for centrifugation. The contents of the large flasks were transferred to appropriate-size Erlenmeyer flasks. When the bulk of the octanol had risen to the surface, the upper portion of the mixture (including all of the octanol phase and about 25 ml of the aqueous phase) was divided between two 15-ml Corex tubes; the remaining aqueous phase was discarded. Tubes and contents were centrifuged at 30,000xg for 20 minutes at 24°C. If the interface between the two phases was not clear, centrifugation was repeated. The octanol phases were sampled (10 µl in triplicate) for liquid scintillation counting, and then carefully removed and returned to their original Erlenmeyer flasks.

All residual octanol, with some water phase, if necessary, was removed from the centrifuge tubes and discarded. The aqueous phases were carefully sampled (1.0 ml in triplicate) for liquid scintillation counting; during this sampling, pipettes were wiped free of any residual octanol. The remaining portions of the aqueous phases were carefully transferred to clean vials in preparation for degradation checks, if necessary.

The octanol-water partitioning coefficient (Kow) for each partitioning was calculated by dividing the dpm/ml of octanol phase by the dpm/ml of aqueous phase. The partitioning procedure was repeated with fresh octanol-saturated water until the Kow values remained constant (indicative of compound purity in the octanol phase).

Once the Kow values for the partitioning of a compound had become constant, the octanol phase was analyzed for the presence of degradation products by the procedure outlined in Section 5.4.2. In all cases purity of the compound dissolved in the octanol phase was >99%. The aqueous phase saved from the last partitioning was analyzed (by the degradation procedure described in Section 5.4.2) for the percent of radioactivity actually representing the parent compound. The level of radioactivity in the aqueous phase was adjusted accordingly and the Kow value corrected. The octanol-water partition coefficients determined by the above procedure for the 14 compounds in the present study are presented in Table 5.4.

5.3. WATER SOLUBILITY DETERMINATION

Many procedures for determining the water solubilities of organic compounds have been recorded in the literature. Portions of the methods of Haque and Schmedding (45) and Mackay and Shiu (46) were utilized in the present investigation to develop a procedure (Figure 5.2) that gives reproducible results with organic compounds varying from relatively soluble to almost insoluble in water.

A quantity of pure radiolabeled compound representing at least a 10-fold excess (per 900 ml of water) over the predicted solubility level was dissolved or diluted in an appropriate solvent (e.g., acetone) or measured without dilution if already liquid (e.g., acetophenone). For compounds with a predicted low water solubility, such as PAH, the radioactive stock solution was used without the addition of unlabeled compound. For compounds with moderate-to-high water solubility, such as acetophenone or α-naphthol, a

TABLE 5.4. OCTANOL-WATER PARTITION COEFFICIENTS (Kow) OF ENERGY-RELATED ORGANIC POLLUTANTS

Compound	Kow
Pyrene	124,000 ± 11,000
7,12-Dimethylbenz[*a*]anthracene	953,000 ± 59,000
Dibenz[*a,h*]anthracene	3,170,000 ± 883,000
3-Methylcholanthrene	2,632,000 ± 701,000
Dibenzothiophene	24,000 ± 2,200
Acridine	4,200 ± 940
2,2'-Biquinoline	20,200 ± 2,200
13*H*-Dibenzo[*a,i*]carbazole	2,514,000 ± 761,000
Acetophenone	38.6 ± 1.2
1-Naphthol	700 ± 62
Benzidine	46.0 ± 2.2
2-Aminoanthracene	13,400 ± 930
6-Aminochrysene	96,600 ± 4,200
Anthracene-9-carboxylic acid	1,300 ± 180

sufficient quantity of pure unlabeled compound was added to the radioactive stock to avoid producing an aqueous solution with an excessively high (wasteful) level of radioactivity.

The dissolved or liquid compound was divided equally between nine foil-covered screw-capped 250-ml Erlenmeyer flasks, thus providing at least a 10-fold excess per flask over the predicted solubility level. The solution was shell-evaporated (under N_2) on the lower walls of the flasks. One hundred ml of degassed (boiled) ultrapure (>10 megohm/cm) water were added to each flask. Flasks were flooded with N_2, capped, and shaken at moderate speed on a Burrell Wrist-Action shaker at room temperature (24°C). Triplicate flasks were removed at 24, 48 and 72 hours; for all of the compounds in the present study, saturation was achieved within 24 hours. In order to ensure that any increase in solubility was not due to degradation of the parent compound, a

Pure radiolabeled compound
(allow at least 10-fold excess/flask over predicted solubility level)

↓

Dissolve in suitable solvent

↓

Shell-evaporate (under N_2) on lower walls of
several (e.g., 9) foil-covered screw-capped 250-ml Erlenmeyer flasks

↓

Add 100 ml degassed ultrapure (>10 megohm/cm) water to each flask

↓

Flood flasks with N_2

↓

Shake (wrist-action shaker), moderate speed, room temperature

↓

Remove triplicate flasks at 24, 48 and 72 hours
(or later, if saturation level not reached yet)

↓

Filter several successive 5-ml samples from flask
through same 0.2µ Nuclepore filter; save filtrates

↓

Sample each filtrate (1.0 ml in triplicate)
for liquid scintillation counting

↓

Calculate solute concentration in each filtrate in terms of ppm or ppb;
average the values of successive filtrates containing similar solute levels
(disregard any early filtrates reflecting
adsorption of solute onto filter membrane)

↓

Perform degradation check on 10-ml sample from at least one flask each day to
ensure that any increase in solubility is not due to compound degradation

FIGURE 5.2. PROTOCOL FOR DETERMINING THE WATER SOLUBILITY OF A HYDROPHOBIC ORGANIC COMPOUND

10-ml sample from at least one flask each day was analyzed for degradation products by the procedure outlined in Section 5.4.3.

The flask contents were sampled (1.0 ml in triplicate) for liquid scintillation counting. Several successive 5-ml samples from a flask were filtered through the same 0.2μ Nuclepore filter. (For all compounds in this study, 0.2μ and 0.08μ Nuclepore filters gave identical results.) Each filtrate was saved and sampled (1.0 ml in triplicate) for liquid scintillation counting. Sequential filtrations were continued until the level of radioactivity in the later filtrates remained constant. The first two or three filtrates of the series usually contained less radioactivity than the subsequent filtrates, probably because the compound was being adsorbed onto the surface of the filter. For most compounds, the level of radioactivity in the filtrates was less than in the unfiltered solution, probably reflecting the retention of aggregates by the filter.

From the specific activity of the compound added to each flask and the level of radioactivity present in the filtrates, the solute concentration in each filtrate was calculated in terms of μg/ml (parts per million, ppm). For all nine flasks, the values of successive filtrates containing similar solute levels were averaged. The water solubilities determined by the above procedure for the 14 compounds in the present study are presented in Table 5.5.

5.4. DEGRADATION STUDIES

It was noted early in the investigation that most of the compounds were reasonably stable to atmospheric and photooxidation when present in high concentration either in solution or on a sorbing surface. However, these same compounds in dilute solution (e.g., aqueous solution) were much more susceptible to degradation. In addition, even after purification, many of the compounds tended to retain a small percentage of impurity (<3%) that was usually a polar oxidation product and thus tended to stay in the more polar or aqueous phases during any procedure. Because liquid scintillation counting of a radioactive sample does not distinguish between parent compound and contamination or degradation products present in the sample, it was necessary to determine what percentage of the radioactivity actually represented the parent compound. This was especially important for the very slightly soluble compounds where the level of radioactivity in the aqueous phase of either a sorption isotherm determination or an octanol-water partitioning was normally very low in comparison to the level in the soil/sediment or octanol phase. Even if only half of the radioactivity in the aqueous phase represented parent compound, the resulting Kp or Kow value would be double that obtained without correction for degradation. Thus the following procedures were developed.

5.4.1. Sorption Isotherms

5.4.1.1. Soil/Sediment Phases

The soil/sediment phases were monitored for degradation products by means of TLC. A small sample (∿0.5 g) of soil/sediment phase, after centrifugation and removal of the aqueous phase, was suspended in 5 ml of acetone,

TABLE 5.5. WATER SOLUBILITIES OF ENERGY-RELATED ORGANIC POLLUTANTS

Compound	Water Solubility (μg/ml)
Pyrene	0.135 ± 0.013
7,12-Dimethylbenz[*a*]anthracene	0.0244 ± 0.0042
Dibenz[*a,h*]anthracene	0.00249 ± 0.00081
3-Methylcholanthrene	0.00323 ± 0.00017
Dibenzothiophene	1.47 ± 0.14
Acridine	38.4 ± 4.5
2,2'-Biquinoline	1.02 ± 0.12
13*H*-Dibenzo[*a,i*]carbazole	0.0104 ± 0.0041
Acetophenone	5440 ± 71
1-Naphthol	866 ± 31
Benzidine	360 ± 8.0
2-Aminoanthracene	1.30 ± 0.159
6-Aminochrysene	0.155 ± 0.018
Anthracene-9-carboxylic acid	85.0 ± 1.9

shaken well, allowed to stand several minutes, reshaken, and then banded (~0.1 ml) across the origin of half of a 20x20-cm 0.5-mm-thick silica gel G plate. The suspension of another soil/sediment was banded on the other half of the plate. A small amount of unlabeled standard solution was spotted at the origin between the two sample bands, and the plate was developed in the appropriate solvent system (see Table 5.1). The location of the unlabeled standard was visualized under UV light and recorded. One-cm segments from the solvent front to the bottom of the plate were scraped from each sample lane into vials of Aquasol for liquid scintillation counting. The quantity of radioactivity in the segments corresponding to the unlabeled standard was calculated as a percentage of the total radioactivity in the sample lane (half-plate-width). For all compounds in the present study, >99% of the radioactivity present in the soil/sediment phases represented parent compound.

5.4.1.2. Aqueous Phases

The aqueous phases that had been removed from the isotherm tubes after centrifugation and sampling were re-centrifuged at 30,000xg for 20 minutes in preparation for high pressure liquid chromatographic (HPLC) analysis. A Waters HPLC system consisting of a Model 660 Solvent Programmer and two Model 6000A Solvent Delivery Systems was operated in conjunction with a Schoeffel Model FS 970 L.C. Fluorometer for monitoring the eluate from the column. The chromatograph was fitted with a 5-ml injection loop and a μBondapak C_{18} column, and operated at a flow rate of 2 ml/min. Suitable gradient and elution conditions for each compound were established using unlabeled standard solution to locate the appropriate fluorescent peak and a solution of pure radioactive compound to locate the fractions containing the parent compound. A 5-ml aqueous phase sample was injected; the pumps were programmed to deliver 20 ml of water to flush all sample components not adhering to the column from the system. This was followed by the appropriate water-to-methanol gradient to elute the parent compound and any contaminants and degradation products in a reasonable length of time. The water flush was collected as three 6.3-ml fractions and the gradient eluate as multiple 1-ml fractions in vials containing Aquasol for liquid scintillation counting. The quantity of radioactivity in the fractions corresponding to the fluorescent parent peak was calculated as a percentage of the total radioactivity in all of the fractions. The concentration of radioactive components in the isotherm aqueous phase was then corrected to reflect parent compound concentration.

During a period when the HPLC system was non-functional, an alternate procedure for determining the percent degradation in the aqueous phases of acridine isotherms was developed utilizing preparative TLC. Approximately eight 0.5-ml aliquots of the aqueous phase were banded across the origin of a 20x20-cm 0.5-mm-thick silica gel G plate, with gentle but complete drying (heat gun) between and after applications. Unlabeled standard solution was spotted at a few locations across the origin. The plate was developed in benzene:methanol (95:5, v/v) to the scribed solvent front mark. Standard spots were located under UV light and their positions recorded. The plate was scored into horizontal 1-cm-wide segments from the solvent front to the bottom of the plate; each segment was scraped into a separate vial of Aquasol for liquid scintillation counting. The quantity of radioactivity in the segments corresponding to the unlabeled standard spots was calculated as a percentage of the total radioactivity on the plate. The concentration of radioactive components in the aqueous phase was then corrected to reflect parent compound concentration. The degradation study on acridine isotherm aqueous phases was repeated using the HPLC system when it was again functional. The two procedures gave comparable results.

5.4.2. Octanol-Water Partitionings

5.4.2.1. Octanol Phases

The octanol phase of the final partitioning of each compound was monitored for degradation products by means of TLC. A small quantity (∿5 μl) of the octanol phase was spotted along with a small amount of unlabeled standard solution at the origin of a 5x20-cm 0.25-mm-thick silica gel G plate.

The plate was developed in the appropriate solvent system, scraped, and analyzed as indicated above. For all compounds in the present study, >99% of the radioactivity present in the octanol phase represented parent compound.

5.4.2.2. Aqueous Phases

The aqueous phase of the final partitioning of each compound was analyzed for degradation products by HPLC in a manner similar to that used for the analysis of isotherm aqueous phases described earlier in this section. The level of radioactivity in the aqueous phase was adjusted accordingly to reflect parent compound radioactivity before final calculation of the Kow.

5.4.3. Water Solubilities

A 10-ml sample from a solubility flask was extracted with three 5-ml volumes of an appropriate solvent (e.g., ether for PAH, methylene chloride for N-heterocyclic compounds). The volume of the extracted aqueous phase remained at 10 ml; the volume of the extract was recorded. Both the extracted aqueous phase and the extract were sampled in triplicate (1.0 ml for the former, 0.2 ml for the latter) for liquid scintillation counting. The extract was concentrated under N_2 to a small volume (∿1 ml); a small quantity of extract (∿0.02 ml) was spotted along with a small amount of unlabeled standard solution at the origin of a 5x20-cm 0.25-mm-thick silica gel G plate. The plate was developed in the appropriate solvent system, scraped, and analyzed as indicated above. For each compound in the present study, the degradation checks of all flasks yielding similar solubility levels after several filtrations revealed that >98% of the total radioactivity was solvent-extractable, and >98% of the radioactivity in the extract represented parent compound.

SECTION 6

SAMPLE SELECTION AND CHARACTERIZATION

6.1. CRITERIA FOR SAMPLE SELECTION

Sampling sites were chosen by two major criteria: (1) to be in close proximity to and downstream from potential coal gasification sites, (2) to provide a wide range in soil and sediment properties that have been shown to affect the degree of adsorption of organic compounds. Eight sites in the United States have been identified as areas of high potential for gasification development (Map 6.1). These include Jefferson, Harrison and Belmont counties in Ohio; Washington and Greene counties in Pennsylvania; Marshall, Marion and Monongalia counties in West Virginia; Hopkins, Muhlenberg, Webster, Union and Henderson counties in Kentucky; St. Clair, Washington, Saline, Gallatin, Hamilton, Williamson, Perry, Madison, Sangamon, Christian, Macoupin, Montgomery, Bond, Vermilion, Edgar, Knox, Fulton and Peoria counties in Illinois; San Juan county in New Mexico; Big Horn, Rosebud, Powder River and Custer counties in Montana; Campbell and Johnson counties in Wyoming; and Dunn and Mercer counties in North Dakota.

These areas with the exception of sites in New Mexico, Montana and Wyoming are in the Missouri, Mississippi, Illinois, Wabash and Ohio River watersheds. Hence, sample collection was centered on these rivers and their watersheds (Map 6.2). In addition to being in close proximity to or downstream from potential coal gasification sites, these sites also provided a wide variation in properties which have been shown to be related to the capacity of soils and sediments to adsorb various materials. At several sites an effort was made to collect sediment samples as well as soil samples representative of major soils in the corresponding watershed. Locations of each sampling site and some pertinent field notes are given in Table 6.1.

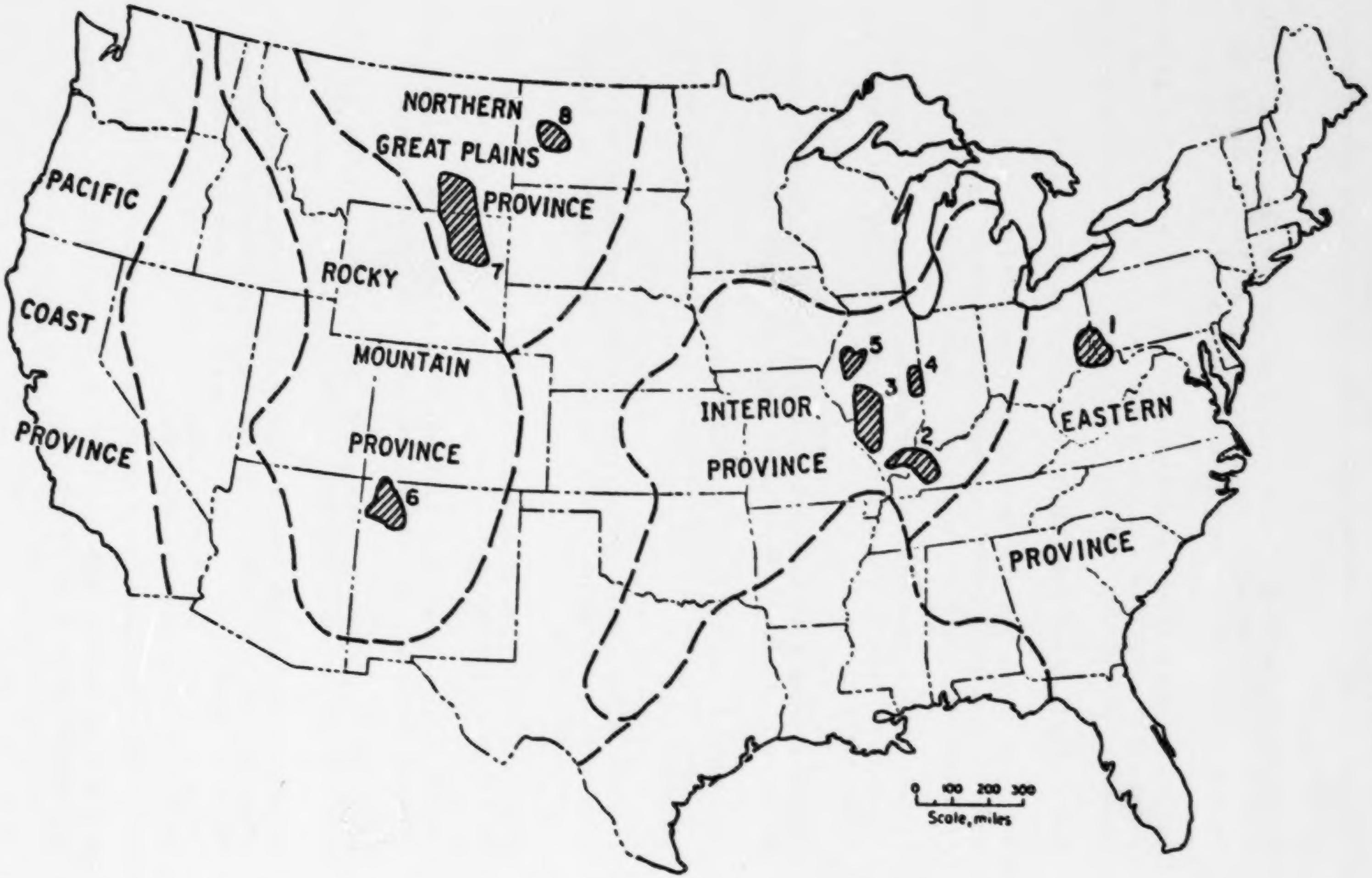
TABLE 6.1. FIELD NOTES

Sample[a]	Notes
EPA-4	Sediment sample from Missouri River, north side of Sakakawea Park. Stanton, North Dakota. Dark-grayish silty material with some fine sand.
EPA-5	Sediment sample from Beaver Creek public use area of Lake Oahe on the Missouri River eighteen miles west of Linton, North Dakota. Appears to be an inundated soil, as sample had noticeable structural development.

TABLE 6.1. FIELD NOTES - *Continued*

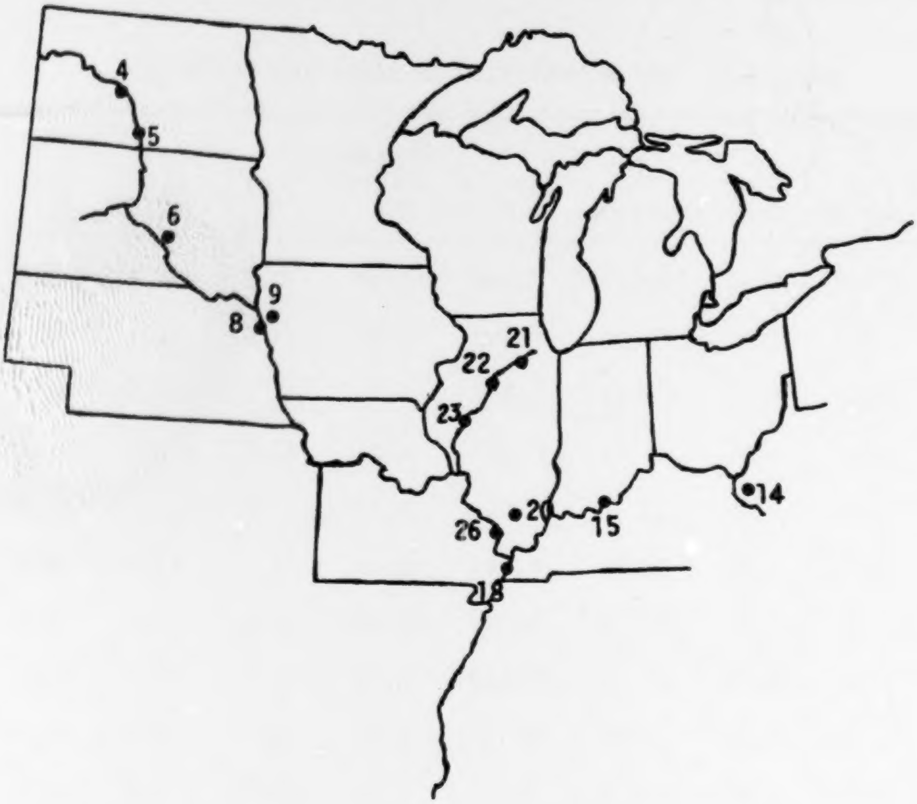
Sample[a]	Notes
EPA-6	Sediment sample from Antelope Creek public use area in lake behind Big Bend Dam on Missouri River, southwest of Pierre, South Dakota. Sample is a grayish clayey material with a fair silt content.
EPA-8	Sediment sample taken from Missouri River near bridge across river, Onawa exit I-29, Iowa side of river. Sample taken next to main channel; high velocity of flow in channel; sample extremely sandy.
EPA-9	Loess sample taken from bluff just north of Turin, Iowa.
EPA-14	Soil taken from a highly eroded red clay hillside southeast of mouth of Big Sandy River near Ohio River. Point Park, Ceredo, West Virginia.
EPA-15	Sediment taken from Ohio River three miles south of Leavenworth, Indiana, at base of steep bluffs in Harrison Crawford State Forest. Silty material.
EPA-18	Sediment taken from half-submerged clay lens in the Mississippi River, next to ferry on Kentucky Route 80, near Columbus, Kentucky.
EPA-20	Soil sample taken from an old field succession, south of scenic overlook exit, Ferne Clyffe State Park, Illinois. Soil series undetermined.
EPA-21	Sediment taken from a small river (creek) feeding Illinois River. Sample taken two miles east of Lorenzo, Illinois, where highway crosses the creek.
EPA-22	Sediment taken from large shallow bay of the Illinois River south of bridge across river at Lacon, Illinois. Silty material.
EPA-23	Sediment taken from Crane Lake north of Blind number 63, Sanganois Wildlife Refuge, confluence of Sangamon and Illinois Rivers.
EPA-26	Sediment from wide side channel of the Mississippi River by private ferry across channel near McClure, Illinois.
EPA-B2	Sediment sample taken from a small stream roughly one-quarter mile below the P-1 watershed on the Southern Piedmont Conservation Research Center (USDA) farm in Oconee County near Watkinsville, Georgia. Stream essentially originates at the terminus of the watershed and drains the watershed.

[a] Samples EPA-4 through EPA-26 collected by W. L. Banwart and J. J. Hassett; sample EPA-B2 collected by D. S. Brown.


PACIFIC
COAST
PROVINCE
NORTHERN
GREAT PLAINS
PROVINCE
ROCKY
MOUNTAIN
PROVINCE
INTERIOR
PROVINCE
EASTERN
PROVINCE
1
2
3
4
5
6
7
8
0 100 200 300
Scale, miles

MAP 6.1. AREAS OF HIGH POTENTIAL FOR COAL GASIFICATION DEVELOPMENT

Modified from *Siting Potential for Coal Gasification Plants in the United States*, by A. E. Lindquist (6).


4
5
6
9
8
21
22
23
20
26
15
14
18

MAP 6.2. SAMPLING SITES ON THE MISSOURI, OHIO, WABASH, ILLINOIS AND MISSISSIPPI RIVER SYSTEMS AND THEIR WATERSHEDS

6.2. SAMPLE CHARACTERIZATION

Table 6.2 gives the pH, cation exchange capacity, percent total nitrogen and organic carbon as well as textural information for the samples collected. Soil reaction, pH, was determined on 1:1 and 1:2 soil-water mixtures by the method of Peech (47). Cation exchange capacity was determined by the ammonium acetate method as modified by Banwart and Hassett (48). Total nitrogen was determined by the method given by Bremner (49) with the exception that the entire digestion sample was distilled rather than an aliquot. Organic carbon was determined by the Walkley-Black method as given by Allison (50). Particle size analysis was determined by the hydrometer method of Day (51) using hydrogen peroxide to destroy the organic matter (52).

TABLE 6.2. CHARACTERISTICS OF SOILS AND SEDIMENTS

	pH (1:1)	pH (1:2)	CEC (me/100g)	Total N (%)	Organic carbon (%)	Sand (%)	Clay (%)	Silt (%)
EPA-4	7.79	8.22	23.72	0.190	2.07	3.0	55.2	41.8
EPA-5	7.44	7.20	19.00	0.192	2.28	33.6	31.0	35.4
EPA-6	7.83	8.23	33.01	0.097	0.72	0.2	68.6	31.2
EPA-8	8.32	8.56	3.72	0.010	0.15	82.4	6.8	10.7
EPA-9	8.34	8.55	12.40	0.015	0.11	7.1	17.4	75.6
EPA-14	4.54	4.30	18.86	0.064	0.48	2.1	63.6	34.4
EPA-15	7.79	7.80	11.30	0.092	0.95	15.6	35.7	48.7
EPA-18	7.76	7.79	15.43	0.062	0.66	34.6	39.5	25.8
EPA-20	5.50	5.16	8.50	0.126	1.30	0	28.6	71.4
EPA-21	7.60	7.95	8.33	0.157	1.88	50.2	7.1	42.7
EPA-22	7.55	7.90	8.53	0.128	1.67	26.1	21.2	52.7
EPA-23	6.70	7.10	31.15	0.195	2.38	17.3	69.1	13.6
EPA-26	7.75	8.10	20.86	0.152	1.48	1.6	42.9	55.4
EPA-B2	6.35	6.50	3.72	0.073	1.21	67.5	18.6	13.9

6.2.1. Instrumental Neutron Activation Analysis (INAA)

The basic concept of INAA is that a small fraction of the stable nuclei present in a sample becomes radioactive when bombarded with neutrons in the 1.5 MW TRIGA reactor. In many of the subsequent radioactive decay processes, one or more high energy photons or gamma rays are emitted. A high resolution semiconductor detector interacts with a gamma ray and yields a pulse with the maximum voltage of the pulse being proportional to the gamma ray energy. This pulse is amplified and shaped and then sorted by a pulse height analyzer so that various energy gamma rays result in counts in different locations in a computer-like memory. The energy of a gamma ray is unique to a particular isotope of a specific element so that a qualitative analysis can be made by observing the spectrum of gamma ray energies emitted by the activated samples. A quantitative analysis can be made by relating the number of gamma rays emitted by the sample relative to a standard containing a known amount of that element.

Approximately 100 mg of the solid sample are weighed out into a precleaned polyethylene container. A standard is prepared by pipetting a small known quantity of an aqueous solution containing a known concentration of the element of interest onto a Whatman No. 41 filter in a clean polyethylene container. The standard is irradiated simultaneously with the sample. The gamma ray spectra from a series of samples and standards are recorded on magnetic tape. A fully automatic computer code then reduces the counting data to elemental concentrations. A list of elements and their interference-free limits of detection is given in Table 6.3. Table 6.4 gives the results of INAA analysis of the soil and sediment samples.

6.2.2. Clay Mineral Analysis

Twenty-gram samples of the soils and sediments were pretreated with 200 ml of NaOCl (pH 9.5) to remove organic matter according to the method of Anderson (53). Samples were placed in a nearly boiling water bath and constantly stirred until the reaction was complete. The suspension was centrifuged at 5,000 rpm for 5 minutes and the supernatant decanted. The solid residue was then treated with 200 ml of 1N NaOAc (pH 5) and placed in a nearly boiling water bath for one hour to facilitate removal of the carbonate cementing agents. The solid residue after centrifugation and decantation of the supernatant was treated by the method of Mehra and Jackson (54) using 160 ml of 0.3M sodium citrate, 20 ml of 1M $NaHCO_3$ and 2 grams of solid sodium dithionate to remove the amorphous cementing agents.

A portion of the residue remaining after removal of the organic matter, carbonates and amorphous materials was saturated with Mg^{2+} ions to facilitate uniform interlayer water adsorption of the expandable layer-silicates. A second portion of the residue was saturated with K^+ ions, thus restricting water adsorption by the normally expandable layer-silicate vermiculite. These K^+ and Mg^{2+}-treated samples were then washed twice with methanol and twice with acetone to remove excess salts.

TABLE 6.3. ELEMENTAL LIMITS OF DETECTION BY INSTRUMENTAL NEUTRON ACTIVATION

ELEMENT	INAA (μg)
Aluminum	0.004
Antimony	0.007
Arsenic	0.005
Barium	0.02
Bismuth	---
Bromine	0.003
Cadmium	0.005
Calcium	4.
Cerium	0.2
Cesium	0.001
Chlorine	0.05
Cobalt	0.01
Copper	---
Dysprosium	0.00003
Europium	0.0001
Gallium	0.002
Gold	0.0005
Hafnium	0.0006
Indium	0.00006
Iodine	0.002
Iridium	0.0003
Iron	2.
Lanthanum	0.005
Lead	---
Magnesium	0.5
Manganese	0.0001
Mercury	0.003
Molybdenum	0.1
Nickel	0.7
Niobium	3.
Potassium	0.2
Rubidium	0.02
Samarium	0.001
Scandium	0.001
Selenium	0.01
Sodium	0.004
Strontium	0.005
Tantalum	0.1
Terbium	0.03
Thallium	---
Thorium	0.2
Titanium	0.1
Tungsten	0.004
Uranium	0.003
Vanadium	0.002
Zinc	0.1
Zirconium	0.8

TABLE 6.4. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF SOILS AND SEDIMENTS

	EPA-B2 (μg/g)	EPA-4 (μg/g)	EPA-5 (μg/g)	EPA-6 (μg/g)	EPA-8 (μg/g)	EPA-9 (μg/g)	EPA-14 (μg/g)
As	<17	5.2	11.8	12.9	9.8	4.6	9.9
Ba	383	671	788	1183	830	872	450
Br	<2.2	<2.6	<3.4	<3.0	<1.9	<2.3	-
Ce	84	59.8	61.3	55.1	41.1	65.9	86.9
Co	8.2	12.45	8.89	19.11	5.96	10.88	11.00
Cs	1.5	4.55	3.24	4.62	1.27	2.98	7.97
Dy	4.1	3.45	3.83	<0.8	2.10	3.17	4.49
Eu	1.22	0.948	1.026	1.020	0.304	1.296	0.943
Ga	12	6.7	10.8	5.7	7.2	8.7	22.9
Hf	10.4	5.22	7.49	6.13	7.81	12.25	8.03
Hg	-	-	-	-	-	-	-
La	40.4	31.2	25.4	33.8	21.6	30.6	46.1
Lu	0.37	0.62	0.38	-	-	-	-
Mn	1140	818.8	392.1	4300	347.8	764.8	216.1
Nd	27	24	36	19.0	31	53	43
Ni	-	-	-	-	-	-	-
Rb	72	80.0	66.7	105	62.4	97	200
Sb	0.18	1.31	6.78	2.14	0.51	1.25	6.05
Sc	7.58	11.52	7.662	9.349	3.739	6.895	16.15
Se	<0.4	0.44	1.53	1.19	<0.19	0.89	1.88
Sr	<78	43	171	338	260	299	<80
Ta	0.66	0.83	0.540	0.48	0.314	0.54	1.08
Tb	1.0	0.68	0.64	0.70	0.460	0.368	0.959
Th	10.9	9.03	8.65	8.25	5.74	9.47	14.61
U	2.6	-	-	-	-	-	-
Yb	2.54	1.841	2.110	1.850	1.424	2.64	2.93
Zr	271	40	102	174	410	37	249
	%	%	%	%	%	%	%
Ca	0.84	2.02	1.41	1.44	1.39	3.08	0.51
Fe	2.18	3.100	2.508	3.039	1.257	2.300	4.888
K	1.00	1.778	1.657	1.331	1.324	1.455	2.453
Na	0.771	0.7556	1.081	0.6590	1.051	0.922	0.1529

TABLE 6.4. *Continued*

	EPA-15 (μg/g)	EPA-18 (μg/g)	EPA-20 (μg/g)	EPA-21 (μg/g)	EPA-22 (μg/g)	EPA-23 (μg/g)	EPA-26 (μg/g)
As	7.4	9.5	4.7	<16	<16	8.1	<26
Ba	451	466	774	349	415	544	595
Br	-	-	-	<2.4	<2.8	10	5.4
Ce	90.1	75.6	76.4	7.9	40.2	63.0	73.3
Co	20.21	14.63	14.83	10.7	8.2	10.8	11.1
Cs	3.95	3.81	2.27	3.7	2.4	5.8	5.0
Dy	5.81	4.92	4.63	3.2	3.7	3.9	5.4
Eu	1.549	1.163	1.575	0.77	0.96	1.14	1.26
Ga	7.1	13.6	<3.1	9.4	<4.2	16	<4.8
Hf	15.63	9.50	14.23	4.7	6.9	2.0	7.3
Hg	-	-	<0.030	-	-	-	-
La	43.5	38.9	38.6	26.4	24.2	26.8	37.8
Lu	-	1.28	-	0.32	0.77	0.16	0.29
Mn	1197	1205	2322	556	727	695	1102
Nd	36	34	44	9.9	30	34	25
Ni	-	-	-	-	-	-	-
Rb	115	73	95	96	74	140	103
Sb	<0.48	0.82	0.26	0.38	1.1	0.52	0.94
Sc	10.97	8.542	5.582	7.75	6.06	12.41	9.60
Se	1.75	1.31	0.30	<0.5	1.5	<0.5	1.0
Sr	272	<103	<164	<66	303	<67	363
Ta	1.37	0.69	0.532	0.57	0.31	0.72	0.96
Tb	0.734	0.63	0.53	0.53	0.59	<0.05	0.83
Th	12.50	9.22	9.92	7.3	6.4	11.2	11.2
U	-	-	-	1.5	<0.6	1.2	4.4
Yb	3.33	2.21	2.55	1.73	1.96	1.49	2.52
Zr	524	254	-	<62	248	139	185
	%	%	%	%	%	%	%
Ca	1.18	0.89	<0.14	1.66	2.83	1.34	1.36
Fe	3.607	2.804	1.626	2.46	2.16	3.70	2.71
K	1.860	1.641	1.73	1.96	1.51	1.74	1.9
Na	0.4682	0.5233	0.7319	0.625	0.71	0.327	0.78

Parallel oriented specimens were prepared using the method of Theisen and Harward (55). Prepared specimens were subjected to X-ray diffraction analysis. A Phillips-Norelco X-ray diffractometer equipped with a digital stepping motor was used. X-rays were detected by a NaI scintillation detector; signals were analyzed, digitized and interfaced to a T.I. ASR 733 perminal using a Canberra model 654 Datanum system.

Diffractograms for the 14 samples were run using the Mg^{2+}-saturated slides to obtain relative amounts of different clay minerals present (Table 6.5). The relative amounts of montmorillonite or vermiculite, illite and kaolinite were determined by calculating the area under their respective peaks on the diffractograms. To further identify the crystalline clay minerals present and to semiquantitatively determine the amount of the various minerals present, step scanning was used over a range of 6 to 20 angstroms. In the step scanning mode, counts were accumulated for 10 seconds at step size increments of 0.01° (2Θ). Data were accumulated on magnetic tape for computer analysis.

TABLE 6.5. QUALITATIVE DETERMINATION OF THE DIFFERENT CLAY MINERALS[a] IN THE LESS-THAN-2μ FRACTION OF THE SOIL AND SEDIMENT SAMPLES

Sample	Montmorillonite or Vermiculite	Illite	Kaolinite	Total Clay[b] (%)
B2	T	T	D3	18.6
4	D3	T	T	55.2
5	D4	T	T	31.0
6	D4	T	T	68.6
8	D4	T	T	6.8
9	D4	T	T	17.4
14	D1	D1	D2	63.6
15	D1	D1	D2	35.7
18	D3	T	T	39.5
20	D3	T	T	28.6
21	D1	D1	D1	7.1
22	D3	T	D1	21.2
23	D4	T	T	69.1
26	D4	T	T	42.9

[a] T = <20% of total clay; D1 = 20-40%; D2 = 40-60%; D3 = 60-80%; D4 = 80-100%.

[b] From Table 6.2.

Because the initial diffractograms obtained were for Mg^{2+}-saturated air-dried samples, additional analysis was necessary to positively identify the minerals present. For example, a diffraction spacing of ∿14Å on Mg^{2+}-saturated slides may be due to the presence of montmorillonite, vermiculite or chlorite or a mixture of these species. Positive identification of montmorillonite, a swelling 2:1 layer-silicate, was obtained by treating the clay sample with ethylene glycol resulting in a shift of the 14-15Å peak to 17Å. The shift is due to penetration of the ethylene glycol into the clay interlayer which results in expansion of the interlayer. Because vermiculite and chlorite would be expected to give essentially identical results with their Mg^{2+}-saturated slides, positive identification of these minerals was accomplished using the K^{+}-saturated samples. The diffraction peak of heated K^{+}-saturated slides occurs at 10Å for vermiculite and at 14-15Å for chlorite.

Illite was identified by a first order peak at 8.9 to 10.5Å and a second order peak at 4.5Å (56). Kaolinite was by far the dominant mineral in some samples such as EPA-B2 and was identified by a 7.0 to 7.2Å peak (57). This peak was positively identified by its disappearance upon heating the Mg^{2+}-saturated specimen to 500°C. Table 6.6 gives the results of the step scores in terms of a semiquantitative determination of amounts of kaolinite, illite and vermiculite or montmorillonite present.

6.2.3. Amorphous Al, Fe and Si

Amorphous mineral colloids occur extensively in soils (58). The commonly used methods of characterizing them is based upon their relative resistances to dissolution in various alkaline solutions. Amorphous Al and Si were extracted in 0.5M NaOH. One-gram samples of the soils or sediments were placed in stainless steel beakers and heated in a constant temperature water bath at 95°C for five minutes. After cooling, the suspensions were brought to exactly 100-ml volume with NaOH. Silica was determined by molybdenum blue color development. Aluminum was determined by atomic absorption spectroscopy (Perkin Elmer model 305b) using a nitrous oxide acetylene flame.

Iron was extracted with buffered citrate-dithionate solution. The procedure used for extractable Fe was essentially that of Mehra and Jackson (54) with the following modifications. Samples were placed in an 80°C water bath after addition of the extracting solution for exactly 5 minutes, followed by the addition of 1 gram of dithionate powder and an additional 15-minute reaction time.

Amorphous silica ranged from 0.09 to 0.44 percent, amorphous aluminum ranged from 0.01 to 0.25 percent, and amorphous iron ranged from 0.22 to 1.38 percent (Table 6.7).

A simple correlation of selected sediment and soil properties is given in Table 6.8. It is interesting to note that CEC is significantly correlated with total clay but not with organic carbon. As would be expected, pH is negatively correlated with amorphous Fe and Al although more than half of the samples collected had pH values greater than 7. While organic carbon does not correlate with CEC, it is significantly correlated with total N, as would be expected.

TABLE 6.6. SEMIQUANTITATIVE DETERMINATION OF CLAY MINERALS IN THE SOILS AND SEDIMENTS.

Sample	Montmorillonite or Vermiculite (%)	Illite (%)	Kaolinite (%)
B2	2.0 (V)[a]	2.7	13.9
4	40.1 (M)	5.7	9.4
5	25.7 (M)	1.8	3.5
6	60.8 (M)	4.6	3.2
8	6.1 (M)	0.2	0.5
9	16.3 (M)	0.4	0.7
14	13.8 (V&M)	12.8	37.0
15	10.1 (V&M)	10.4	15.2
18	29.7 (M)	2.8	7.0
20	21.9 (M)	2.1	4.6
21	2.8 (M)	1.6	2.7
22	14.8 (M)	2.1	4.3
23	57.6 (M)	4.2	7.3
26	37.1 (M)	1.7	4.1

[a] (V) = vermiculite; (M) = montmorillonite.

TABLE 6.7. SODIUM HYDROXIDE-EXTRACTABLE Si AND Al AND CITRATE-DITHIONATE-EXTRACTABLE Fe IN THE SOIL AND SEDIMENT SAMPLES

Sample	Si (%)	Al (%)	Fe (%)
B2	0.12	0.25	0.88
4	0.18	0.07	0.71
5	0.12	0.03	0.49
6	0.44	0.03	0.59
8	0.08	0.01	0.22
9	0.26	0.02	0.59
14	0.10	0.20	1.38
15	0.09	0.10	1.27
18	0.10	0.05	0.74
20	0.16	0.14	0.61
21	0.12	0.05	0.60
22	0.09	0.05	0.61
23	0.21	0.12	0.73
26	0.29	0.13	0.63

TABLE 6.8. CORRELATION MATRIX OF SELECTED SAMPLE CHARACTERISTICS

							AMORPHOUS	
		pH	CEC	%N	%OC	%Clay	%Si	%Fe
	CEC	0.002						
	%N	-0.076	0.470					
	%OC	-0.063	0.304	0.964[b]				
	%Clay	-0.318	0.898[b]	0.344	0.181			
AMORPHOUS	%Si	0.223	0.678[b]	0.097	-0.062	0.484		
	%Fe	-0.559[a]	0.090	-0.063	-0.105	0.419	-0.215	
	%Al	-0.774[b]	-0.106	0.037	0.077	0.218	-0.164	0.631[b]

[a] Significant at 5% level

[b] Significant at 1% level

6.3. EFFECT OF SAMPLE PRETREATMENT ON SORPTION OF ACETOPHENONE BY SEDIMENTS

Sediment or soil samples can be handled various ways from the time they are collected until laboratory analyses are performed. Probably the most commonly used pretreatment method is to air-dry samples and pass them through a 2-mm sieve prior to storage and subsequent treatment or analysis. Samples are sometimes oven-dried or freeze-dried to "preserve" the integrity of the sample and/or for the convenience of the experimenter.

While the effect of sample pretreatment on the sorption of acetophenone has not been reported, several studies have shown sample pretreatment to have significant effects on soil physical and/or chemical properties, such as levels of available nutrients in soils (59,60,61,62). Thien *et al.* (63), for example, reported that soil pretreatment significantly affects pH, nitrate nitrogen, extractable micro and macronutrients but not organic carbon or clay mineralogy. Sertsu and Sanchez (62) concluded that heating at 200°C did not alter clay mineralogy but did result in some organic carbon decomposition and changes in soil pH and extractable nutrients.

Soil samples are commonly ground or crushed to pass a 2-mm sieve after drying and prior to storage for analysis. For certain chemical tests such as total carbon, however, soils are often ground to pass a 60-mesh sieve prior to analysis. Data by Soltanpour *et al.* (64, 65) show that both grinding force and grinding time played a significant role in DTPA micronutrient soil tests but the effect of grinding fineness on sorption of acetophenone or other organic compounds has not been reported.

Acetophenone was employed as a test compound for this study. It represents one class of compounds, aromatic ketones, which have been shown to be present in coal gasification wastes. These wastes represent a potential for adding a wide variety of organic substances to the environment. Results of this study were needed to evaluate the use of air-dried soil and sediment samples in sorption studies.

Khan *et al.* (16) reported that sorption of acetophenone was highly correlated with organic carbon content of soil and sediment samples whereas other chemical or physical properties determined were not. They also speculated that the amount and type of clay might be important in samples where organic carbon was low. Sorption of certain pesticides is highly dependent on the amount of organic matter in soils (66,67,68,69,70,71).

The purpose of this study was to examine the effect of (a) sample pretreatment, (b) extent of grinding, and (c) organic matter destruction on sorption of acetophenone by soils and sediments.

6.3.1. Experimental Methods

The Crane Island and Sangamon samples (Table 6.9) were collected from the Illinois River near Crane Island and from the Sangamon River near Mahomet, Illinois. Bulk samples were removed, mixed by hand, cooled to 2°C and taken immediately to the laboratory. Samples were mechanically mixed and subdivided

TABLE 6.9. SELECTED CHEMICAL AND PHYSICAL PROPERTIES OF RIVER SEDIMENTS.

Sample	Organic Carbon (%)	Silt (%)	Total Clay (%)
Sangamon	2.08	48	35
Crane Island	3.16	12	69

for further experimentation. One subsample was stored at 2°C, a second subsample frozen, a third subsample air-dried, a fourth subsample freeze-dried, and a fifth subsample oven-dried at 110°C for 48 hours. Air-dried, freeze-dried, and oven-dried samples were ground to pass a 2-mm sieve and stored for further analysis.

In a second study, another air-dried sample was subdivided and portions ground to pass through 2, 0.6 and 0.25-mm sieves to examine the effect of particle size on sorption of acetophenone.

In a third study designed to examine the effect of organic matter removal on sorption of acetophenone, 14 additional soil and sediment samples described in Section 6.2 were air-dried and ground to pass a 2-mm sieve.

Organic matter was removed from these samples by treatment with NaOCl (pH = 9.5) according to the method of Anderson (53). The samples were then washed with deionized water and subsequently saturated with calcium. After calcium saturation the samples were air-dried and ground to pass a 2-mm sieve. Organic carbon determinations were performed by the Walkley and Black method (50) on both the original air-dry samples and on samples after treatment to remove organic matter.

Batch equilibrium sorption isotherms were determined for samples stored at 2°C, frozen, air-dried, freeze-dried, and oven-dried to examine the effect of sample processing and sample pretreatment. Similar isotherms were run on air-dried samples ground to three different mesh sizes and on the fourteen samples before and after treatment with NaOCl to remove organic matter. Radiolabeled ^{14}C-acetophenone (99% pure) obtained from ICN Pharmaceuticals Inc. and unlabeled acetophenone (99% pure) from Eastman Kodak Co. were used for adsorption studies. Purity was verified using thin-layer chromatography. A stock solution (4154 µg/ml) was prepared in ultrapure distilled water. A minimum of triplicate adsorption isotherms were determined using 2:5 solid to solution ratio with initial concentrations varying from 138 to 1108 µg/ml. The isotherms were run in stainless steel centrifuge tubes (teflon-covered lids) in a temperature-controlled shaking water bath at 25°C for 24 hours. Initial and final concentrations of acetophenone in the solution phase were determined using a Packard Model 3330 liquid scintillation spectrometer. The concentration of acetophenone in the soil/sediment phase (μg/g) was determined by difference.

6.3.2. Results and Discussion

6.3.2.1. Sample Pretreatment

Sorption of acetophenone on fresh (2°C), frozen, air-dried, freeze-dried and oven-dried samples in the sample pretreatment study followed a linear trend exemplified by sample isotherms shown in Figure 6.1. The sorption isotherms gave a good fit to the modified Freundlich equation:

$$Cs = Kp \cdot Cw \tag{4-1}$$

where Cs is the amount adsorbed on the sediment in μg/g, Cw is the equilibrium concentration in μg/ml, and Kp is the linear partition or sorption constant. The correlation coefficient (r^2) between Cs and Cw was determined for individual pretreatments and ranged from 0.98 to 1.00 for the five pretreatments tested. These correlations support the observation of linearity of isotherms obtained for acetophenone sorption on soils and sediments by Khan *et al.* (16).

The Kp values for the sample pretreatment studies are shown in Table 6.10. Individual Kp values ranged from 0.84 to 1.07 for Sangamon samples and from 0.90 to 1.09 for Crane Island samples but no consistent trends could be associated with any of the sample pretreatment techniques studies. The Kp for the oven-dried Sangamon sample appeared to be slightly lower (0.84) than the Kp for fresh, frozen, air-dried, or freeze-dried but the difference was not significant at the 5% level of probability. The mean Kp values for the two sediments studied ranged from 0.97 to 1.03 with none of the individual sample pretreatment techniques resulting in Kp values significantly different from the others.

TABLE 6.10. EFFECT OF SAMPLE PRETREATMENT ON MODIFIED FREUNDLICH PARTITION COEFFICIENTS (Kp).

Sample	Kp				
	Fresh	Frozen	Air-dried	Freeze-dried	Oven-dried
Sangamon	1.07	1.07	0.95	0.92	0.84
Crane Island	0.90	0.99	1.04	1.09	1.09
Mean[a]	0.98	1.03	1.00	1.01	0.97

[a] Means are not significantly different at the 5% level.

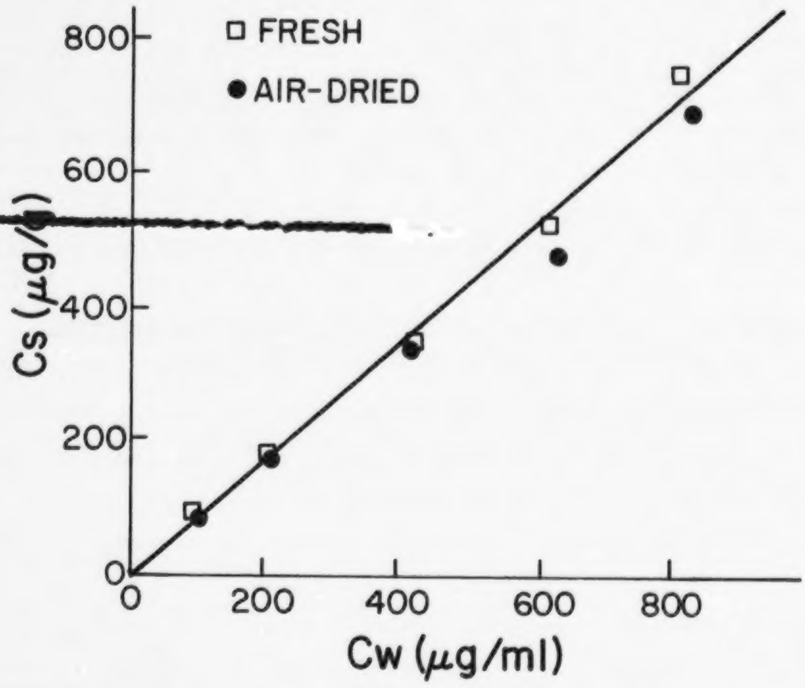


FIGURE 6.1. COMPARISON OF ISOTHERMS FOR THE SORPTION OF ACETOPHENONE BY FRESH AND AIR-DRIED SAMPLES OF CRANE ISLAND SEDIMENT

Since organic carbon content has been shown to be the dominant soil characteristic on which acetophenone sorption depends (16), organic carbon determinations were carried out on each of the pretreatment subsamples used for isotherm analysis. The organic carbon content was nearly identical for all pretreatments except oven-drying. The organic carbon content, as measured by the Walkley-Black method, in the oven-dried samples was 0.4 and 0.1 percent lower for the Crane and Sangamon samples, respectively. Thus, while oven-drying had the greatest effect on the organic carbon content of the Crane sample, this was not reflected in the Kp of this sample.

For ease of storage or handling, air-dried samples are commonly used in sorption studies. The results of these studies imply that sorption of acetophenone by air-dried samples is very similar to that by samples in their natural or fresh condition and samples that have been frozen or freeze-dried. Thus laboratory pretreatment of the kind tested here appears to have no significant effect on the sorption of this compound.

6.3.2.2. Effect of Extent of Grinding

A separate air-dried subsample of two sediments was used to examine the effect of extent of grinding on sorption of acetophenone. These results (Table 6.11) show that samples ground to pass through a 2-mm maximum diameter sieve (10-mesh) had approximately the same Kp values as those ground to pass through a 0.6 or 0.25-mm maximum diameter (30 or 60-mesh) sieve. The Kp values obtained for each treatment were not different at the 5% level of probability. While the extent of grinding did not appreciably affect sorption of acetophenone, it may serve to decrease subsample variability for soil chemical analysis.

TABLE 6.11. EFFECT OF EXTENT OF GRINDING ON SORPTION (Kp) OF ACETOPHENONE

	Mesh size of sieve to pass sample		
Sample	10 (2 mm)	30 (0.6 mm)	60 (0.25 mm)
Sangamon	0.99	0.88	0.91
Crane Island	0.99	1.13	1.11
Mean[a]	0.99	1.01	1.01

[a] Means are not significantly different at the 5% level.

6.3.2.3. Organic Matter Removal

Treatment with NaOCl was very effective in oxidizing organic matter for the 14 samples studied (Table 6.12). Analysis indicated approximately 95% reduction in organic carbon content for most samples, and no sample contained more than 0.11% organic carbon after treatment. Organic matter removal followed by calcium saturation of the samples decreased Kp values for samples initially containing more than 1% organic carbon and increased Kp values for samples containing less than 1% organic carbon before treatment.

TABLE 6.12. ORGANIC CARBON CONTENTS AND MODIFIED FREUNDLICH PARTITION COEFFICIENTS (Kp, 1/n=1) BEFORE AND AFTER ORGANIC MATTER REMOVAL, AND EXPANDABLE (2:1) CLAY MATERIAL IN SOIL AND SEDIMENT SAMPLES.

Sample	Organic Carbon (%)		Kp		2:1 expandable clay (%)
	before treatment	after treatment	before treatment	after treatment	
4	2.07	0.11	0.89	0.65	40
5	2.28	0.04	0.56	0.49	26
6	0.72	0.07	0.68	0.94	61
8	0.15	0.02	0.07	0.28	6
9	0.11	0.03	0.09	0.31	16
14	0.48	0.04	0.12	0.28	14
15	0.95	0.04	0.27	0.29	10
18	0.66	0.03	0.30	0.33	30
20	1.30	0.02	0.29	0.25	22
21	1.88	0.06	0.85	0.33	3
22	1.67	0.09	0.53	0.30	15
23	2.38	0.03	0.68	0.44	58
26	1.48	0.11	0.66	0.29	37
B2	1.21	0.01	0.44	0.17	2

Kp values for samples containing large amounts of organic carbon might be expected to decrease upon treatment since organic carbon has been shown to be the major factor controlling sorption of acetophenone (16). The increase in adsorption of acetophenone by samples containing less than 1% organic carbon initially may be partially accounted for by the fact that samples were calcium-saturated after treatment with NaOCl. Calcium had been added to flocculate the soils and sediments insuring a clear solution phase for isotherm analysis. Preliminary data in our laboratory indicate that sorption of acetophenone by otherwise untreated samples increases when samples are calcium-saturated.

Since organic carbon has been shown to be the major factor affecting acetophenone adsorption (16), other soil properties may become significant with organic matter removal. The Kp values were not correlated with the remaining organic matter after NaOCl treatment. The data showed that correlation of Kp with 2:1 expandable clay mineral content was 0.77 and significant at the 1% level of probability when samples had been subjected to organic matter removal. A plot of these data is shown in Figure 6.2. The following regression model was developed using Kp as a dependent variable and 2:1 expanding clay content (Y) as an independent variable.

$$Kp = 0.19 + 0.008\,Y \tag{6-1}$$

Other workers have reported that swelling clay minerals are important constituents for sorption of pesticides (12,72,73,75). The correlation of Kp with total clay was also significant (0.59) but at the 5% level largely because % total clay is correlated, as expected, with swelling clay. However, clay type is extremely important, as exemplified by samples 6 and 14. These two samples contain approximately the same amount of clay (total) but sample 6 (Kp = 0.94) contains more than 4 times as much montmorillonite as sample 14 (Kp = 0.28) and had a Kp more than 3 times that of sample 14.

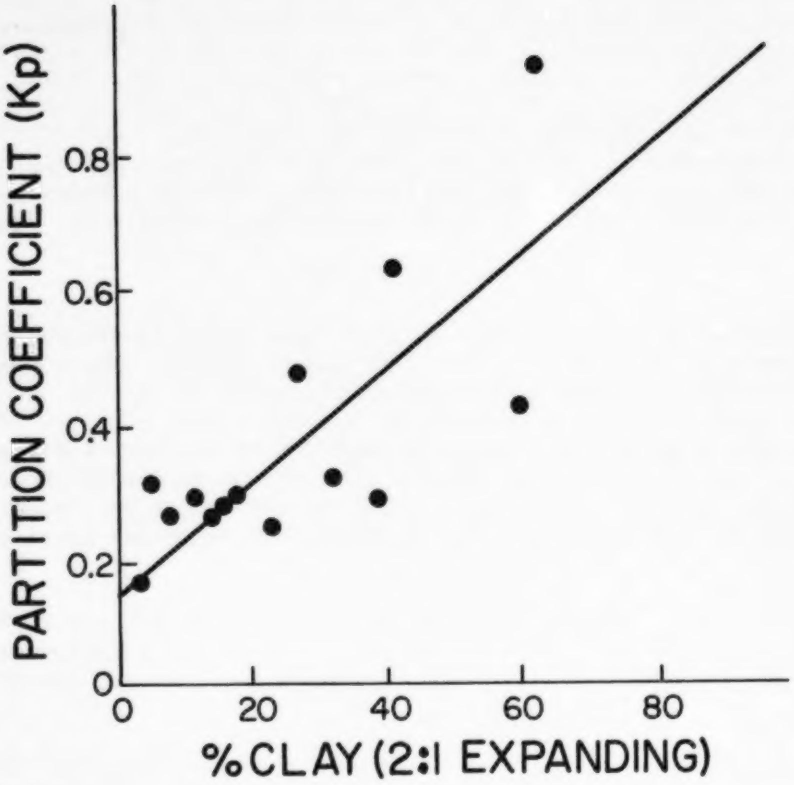


FIGURE 6.2. COMPARISON OF THE LINEAR PARTITION COEFFICIENTS (Kp) FOR THE SORPTION OF ACETOPHENONE BY SOIL AND SEDIMENT SAMPLES AND THE PERCENT CLAY IN THE SAMPLES AFTER ORGANIC MATTER OXIDATION

SECTION 7

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